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Argonne NATIONAL LABORATORY

Shape-Selective Catalysts for Fischer-Tropsch Chemistry: Iron-Containing Particulate Catalysts

Activity Report: January 1, 2001 – December 31, 2004

Chemical Engineering Division

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Shape-Selective Catalysts for Fischer-Tropsch Chemistry: Iron-Containing Particulate Catalysts

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Summary

Argonne National Laboratory is carrying out a research program to create, prepare, and evaluate catalysts to promote Fischer-Tropsch (FT) chemistry—specifically, the reaction of hydrogen with carbon monoxide to form long-chain hydrocarbons. In addition to needing high activity, it is desirable that the catalysts have high selectivity and stability with respect to both mechanical strength and aging properties. It is desired that selectivity be directed toward producing diesel fraction components and avoiding excess yields of both light hydrocarbons and heavy waxes. The goal is to produce shape-selective catalysts that have the potential to limit the formation of long-chain products and yet retain the active metal sites in a protected "cage." This cage also restricts their loss by attrition during use in slurry-bed reactors. The first stage of this program was to prepare and evaluate iron-containing particulate catalysts. This activity report centers upon this first stage of experimentation with particulate FT catalysts. (For reference, a second experimental stage is under way to prepare and evaluate active FT catalysts formed by atomic-layer deposition [ALD] of active components on supported membranes.)

To date, experimentation has centered upon the evaluation of a sample of iron-based, spray-dried catalyst prepared by B.H. Davis of the Center of Applied Energy Research (CAER) and samples of his catalyst onto which inorganic "shells" were deposited. The reference CAER catalyst contained a high level of dispersed fine particles, a portion of which was removed by differential settling.

Reaction conditions have been established using a FT laboratory unit such that reasonable levels of CO conversion can be achieved, where therefore a valid catalyst comparison can be made. A wide range of catalytic activities was observed with SiO_2-coated FT catalysts. Two techniques were used for SiO_2 coating. The first involved a caustic precipitation of SiO_2 from an organo-silicate onto the CAER catalyst. The second was the acidic precipitation of an organo-silicate with aging to form fractal particles that were then deposited onto the CAER catalyst. Several resulting FT catalysts were as active as the coarse catalyst on which they were prepared. The most active ones were those with the least amount of coating, namely about 2.2 wt% SiO_2. In the case of the latter acid technique, the use of HCl and HNO_3 was much more effective than that of H_2SO_4.

Scanning electron microscopy (SEM) was used to observe and analyze as-received and treated FT catalysts. It was observed that (1) spherical particles of CAER FT catalyst were made up of agglomerates of particles that were, in turn, also agglomerates; (2) the spray drying process of CAER apparently concentrated the Si precursor at the surface during drying; (3) while SEM pointed out broad differences in the appearance of the prepared catalyst particles, there was little indication that the catalysts were being uniformly coated with a cage-like protective surface, with perhaps the exception of HNO_3-precipitated catalyst; and (4) there was only a limited penetration of carbon (i.e., CO) into the FT catalyst during the conditioning and FT reaction steps.

Introduction

Fischer-Tropsch (FT) chemistry involves the reaction of hydrogen with carbon monoxide to form long-chain hydrocarbons. Even though this process was invented in Germany in 1923, there has been a continuing development of catalysts, the most common of which are based upon iron, cobalt, and ruthenium. It has been directed by DOE that research in this project center upon iron-containing catalysts with an emphasis on physical strength and catalyst activity.

The available literature on these catalysts is very extensive, and it is beyond the scope of this project to prepare another literature survey. Only recent literature dealing with specific problem areas will be cited when appropriate. For reference, a very comprehensive recent series of articles on the FT process has been edited by Hans Schulz and Michael Claeys[1]; see also C.N. Satterfield[2]. B. H. Davis has carried out an extensive study of FT catalysis under DOE contracts; reference is made to the Final Technical Report[3] of Contract No. PC90056; also note interim reports of PC94055.

Iron is the least expensive FT catalyst. It is typically promoted with alkali (i.e., 0.5 wt% K_2O) for activity and stability. It has been proposed[2] that potassium donates electrons to the iron, weakens the CO bond, strengthens the Fe-C bond, and weakens the Fe-H bond, so the quantity of CO adsorbed increases and that of H_2 decreases. For reference, the fixed-bed reactors at SASOL (South African Synthetic Oil Limited) operate at about 220°C and 2.7 MPa using a precipitated iron catalyst heavily promoted with potassium. Their entrained-bed reactors operate at about 320°C and 2.2 MPa with a reduced fused magnetite catalyst of considerably lower potassium content.

CuO is added to the Fe catalyst to lower the reduction temperature of Fe_2O_3. This addition reduces sintering and apparently does not affect catalyst selectivity. SiO_2 and Al_2O_3 may be added for structural strength; however excessive levels reduce catalyst activity.

Because alkalized iron catalysts demonstrate water gas activity, they are of particular interest when the feed stream has low hydrogen content (i.e., H_2/CO ratio of about 1.0 for coal or heavy oil gasification versus 2.0 for methane gasification). It has been reported[1] that the activity of iron catalysts is affected through the interaction with water. When these iron catalysts are used, water must be removed from recycle streams along with heavy hydrocarbon products. Typical ratios of recycle to fresh feed rates are about 2.

Numerous articles have indicated that iron catalysts are active for FT synthesis only when in the carbide state. A recent review article[4] of Van der Laan and Beenackers provides a good summary of pertinent references; see also Bukur et al.[5] Numerous articles have demonstrated the importance of catalyst pre-conditioning treatment of fresh catalyst with CO to establish the active carbide surfaces; for example, see Shroff et al.[6] The procedure used by Davis[3] is as follows:

> "The catalyst was pretreated in CO; the sample was heated from 110 to 270°C during a period of about 2 (2°C/min) hours and then held at 270°C in a CO flow of 2 NL/g Fe/hr for 22 hours."

The strength of iron-based catalysts is of concern, particularly when used in slurry-bed catalytic reactors. Espinoza et al.[7] of SASOL states, "The main difficulty with the commercial application of the SPR (Slurry Phase Reactor) is the separation of the wax product from the catalyst. This is especially true for the relatively friable precipitated iron catalysts." D. S. Kalakkad et al.[8] studied the attrition and phase transformation of precipitated iron FT catalysts. They found that spray-dried particles (agglomerates) about 30 μm diameter easily fragmented to particles of about 1 μm size. In addition, phase transformation resulted in size reductions to about 20 μm. The recent presentation of Gormley, Deffenbaugh and Zarochark[9] also points out the difficulty of catalyst attrition with the subsequent problems of cleaning up the resulting FT wax product stream.

Interest in this project was directed toward the formation of fractal surface structures that would provide structural strength and yet be porous for the flow of reactants and products to and from the iron-containing catalyst. Again, there is an extensive literature on the formation of fractal structures. The Symposia Proceedings of Brinker et al.,[10] the book of Brinker and Scherer,[11] the collection of manuscripts edited by Klein,[12] and the text of Zallen[13] present a good background of the subject.

The goal of the first stage of this project was to create, prepare, and evaluate catalysts to promote Fischer-Tropsch (FT) chemistry. Emphasis was placed upon iron-containing catalysts that are preferred for syngases having low ratios of H_2/CO. Emphasis was also placed upon shape-selective catalysts that had the potential to limit long-chain products and retain active metal sites in a protected "cage" to restrict their loss during use in slurry-bed reactors.

Experimentation and Results

Experimental

A continuous-flow catalytic-bed unit was modified and used for this FT study. A flow schematic is shown in Figure 1.

The gaseous feed consisted of either a 1:1 molar blend of CO and H_2 or of a 2:1 blend with the addition of H_2. The feed passed through a preheater/reactor that consisted of a 1/2-in.-O.D. (3/8-in.-I.D.) tube of 36 in. length. Gaseous flow was downward through the following zones:

1. An empty (quartz wool) zone to serve as a preheater,
2. Inert packing consisting of low-surface α-Al_2O_3 to ensure radial flow dispersion,
3. Supported catalyst that was mixed with inert filler,
4. Additional α-Al_2O_3 packing, and
5. A bottom zone made up of a low-internal-diameter tube so that the catalyst was retained in the temperature-controlled region of the tube.

The preheater/reactor had a total of six internal and two external thermocouples. The reactor temperature was controlled using the thermocouple at the center of the catalyst bed. The FT experiments were carried out at mid-bed temperatures of either 265° or 285°C, pressures averaging 13.1 MPa (190 psia), a H_2/CO feed molar ratio of 1.0, a gas feed rate of about 40 mL/min, and a catalyst charge of 0.70 g . The gas feed rate was equivalent to a space velocity of 3.4 normal liters

per hour gram (NL/hr-g).

The reactor effluent was cooled in air and then passed through a wet-ice-cooled trap; there was a provision for a dry-ice trap that was not used. The traps were set up for parallel operation so that periodic condensate samples could be recovered for weighing and sampling. The pressure of the off-gas was controlled and subsequently metered and sampled. The gas composition was determined using an HP 6890 Series gas chromatograph (GC) that was modified by LINC Quantum Analytics of Foster City, CA. It had three columns: (1) a molecular sieve column (7 ft x 1/16 in. 13X 45/60) for light gas retention and separation, (2) a capillary column (50 m x 0.53 mm KCl modified Al_2O_3 PLOT) for hydrocarbon analysis by a flame ionization detector (FID), and (3) a packed column (7 ft x 1/16 in. Hayesep A 60/80) for CO_2 separation and analysis using a thermal conductivity detector (TCD).

Catalyst Preparation

A summary of the catalysts is presented in Table 1, and their use in FT experiments is outlined in Table 2.

To establish catalyst familiarity, samples of iron-based FT catalyst were prepared using procedures similar to those reported by Davis.[3] These samples were made by mixing ferric nitrate solution with concentrated ammonia at temperatures of about 55°C. Selected batches also were made with the addition of tetraethylorthosilicate (TEOS) prior to the precipitation with ammonia. Selected samples (DCFT-8 and 10A) were used in FT experimental runs.

Two samples of FT catalyst were obtained from B. H. Davis[3] of CAER. The first consisted of the bulk spray-dryed catalyst designated "RLS 4.4 Si/150 Cyclone Iron Catalyst" (RLS) and the second was freshly prepared catalyst designated "RJO 290 100Fe/4.6Si/1.44K."

Selected CAER catalyst samples were separated by differential settling to isolate fractions of differing particle diameter. It was found that a reasonable procedure was to mix 25 g of RLS catalyst with 225 mL water and 25 mL ethanol. After a mild stirring in a 250 mL graduate for 5 min, the slurry was allowed to settle for 1 min and the top slurry was siphoned down to 50 mL. Water and ethanol (200 and 20 mL, respectively) were added to the bottoms slurry, and the separation procedure was repeated four times. The final slurry was drawn down to 12-15 mL. Selected slurry samples were filtered (Whatman #50). Typical bottoms samples, designated as "coarse," made up about 25-35% of the feed catalyst, and their filter cakes contained about 5% moisture. Microscopic examination indicated that the recovered particles were relatively uniform, with an average size of about 20 microns. Subsequent SEM examination indicated that there remained a moderate amount of catalyst fines, as described in the Results and Discussion section.

The procedure for caustic SiO_2 precipitation and coating was as follows. Selected samples of the above "coarse" and raw (un-separated) CAER catalyst samples were contacted with aqueous/ethanol solutions of TEOS followed by the drop-wise addition of 30 wt% ammonium hydroxide solution (maintaining a pH of about 11.0). This procedure should generate a silica gel coating on the catalyst particles. The depth and thickness of the coating into the particles would have been influenced by the concentrations, rates of addition, etc. Selected blends were also made with limited levels of

tetraethyl ammonium hydroxide (TEOH — 20 wt% in water). The resulting catalyst samples were dried in a vacuum oven and calcined (400°C for 4 hr).

As will be discussed in the following section, fractal silica is reported to be formed by acidic precipitation of organo-silicates along with subsequent slurry aging. Dilute H_2SO_4 was used in catalyst preparations 180A and 178A through 178D. HCl was used in catalyst preparations 183A through 183C, and HNO_3 in 2121-30AA through 30CC.

The first two acid-precipitated catalysts (178A and 178B) were prepared by vigorously mixing solutions of water, H_2SO_4, and ethanol (3.35%, 0.72%, and 95.9%, respectively) and ethanol plus TEOS (97.8% and 2.2%, respectively). The ratios of the first and second solutions were 37.8 and 62.2%, respectively. The resulting mixtures were aged at 25°C for one day. The CAER catalyst was added to 178A, and the slurry was aged for about 5 days at 45°C. The pH of the 178B mixture was adjusted to 10.0 with the addition of NH_4OH after the initial aging period. The CAER catalyst was then added, and the resulting slurry aged in the same manner as 178A. Catalysts 178C and 178D were prepared similarly to 178A, but the levels of TEOS were increased. As a reference sample, catalyst 180A was handled similarly to 178A, but without the addition of TEOS. All of these catalysts were recovered with filtration and calcination at 500°C.

A second series of catalysts (183a through 183C) was prepared using HCl as the acid. The preparation was similar to that given above. The acid solution consisted of HCl, H_2O and ethanol with weight percentages of 0.46, 2.0, and 98.5, respectively. The TEOS was mixed with ethanol and then mixed with the above acid solution (62:38) and handled as described above.

A third series of catalysts (2121-30AA through 30CC) was prepared using HNO_3 as the acid. The acid solution consisted of HNO_3, H_2O and ethanol with weight percentages of 0.663, 3.22 and 96.12, respectively. TEOS was mixed with ethanol, and then mixed with the above acid solution. The relative ratios and contact times are given in Table 1. The catalysts were recovered with filtration and calcination at 500°C.

Results and Discussion

Catalyst Particle Size/Shape Determination

To establish a basis for future experimentation, selected samples of the above catalysts were examined using a JEOL JSM6400 scanning electron microscope. The powder samples were dusted onto carbon conductive tape and coated with gold prior to examination.

The samples prepared at Argonne were highly irregular, and they ranged widely in size (2 through 600 μm). Some of the material was powder in the range of 2 through 14 μm with an average of about 7 μm. There were also large chunks and even solid chips that averaged about 150 μm. It did not appear that there was agglomeration of small particles into large ones. Based upon the observations, it appeared that poor mixing had been used in these preparations.

Considering that the overall project goal was to prepare and evaluate the deposition of "cage-like" shells upon uniform FT catalyst particles, the use of Argonne-prepared catalyst was rejected. Only the CAER-prepared catalyst was used in subsequent runs.

A sample of the spray-dried LSR catalyst was also examined. This material consisted of a blend of fine particles (1-5 μm) and spherical agglomerates in the range of 20-40 μm. This is consistent with a description by B.H. Davis that spray-drying had not been as effective as desired. There remains the question of whether the level of small particles was due to the operation of the spray-drying unit or to subsequent break-up of the larger particles. Considering the particle size distribution, it is probably the former.

The sample of freshly prepared CAER catalysts designated "RJO 290 100Fe/4.6Si/1.44K" was also scanned using the SEM. This catalyst was irregular in size ranging between 2 and 30 μm. Because the LSR catalyst was more uniform, subsequent experimentation was limited to using this catalyst.

Use of Iron-Containing Catalysts in FT Experiments

The iron-containing catalysts were tested using the above procedure. The results of these runs are included here as Figures 2 through 12 and Tables 3 through 8.

a. α-Alumina

The first FT experiment was undertaken using the preheater and reactor charged with only α-Al_2O_3 to ensure that there was no or only limited background catalytic activity due to the "inert" filler. Runs 85A, 85C, 87C and 85F were made at mid-bed temperatures ranging between 265 and 290°C with the other conditions listed above. As shown in Table 3, there was only a nominal level (<0.05%) of methane generated in one of the above runs; 0.02 % and less was observed in the other runs. These levels are indicative of background error apparently caused by GC switching at about the column elution time. No other hydrocarbons or carbon dioxide were detected at levels at or above 0.01%. In summary, the α-Al_2O_3 was essentially inert at the established reaction conditions.

b. As-received CAER Catalyst

As-received CAER FT catalyst was used in Runs 100 and 101, made at 268 and 284°C, respectively. The results are summarized in Table 3 and Figures 2 and 6. This catalyst was active with 35 and 57% CO conversion levels at mid-bed temperatures of 268° and 284°C, respectively. Based upon an overall carbon material balance, the selectivity of converted CO to hydrocarbons averaged 56%, with the remainder forming CO_2.

Experiments with the coarse CAER catalyst, designated 72 CAER, were carried out at reaction temperatures between 267°and 290°C. As shown in Table 3 and Figures 2 and 6, the activity of the 72 CAER catalyst was equivalent to as-received CAER catalyst with the exception that nominally more CO_2 was generated with the 72 CAER catalyst.

c. SiO_2- Surface Coated CAER Catalysts Using Caustic Precipitation Techniques

The 77B catalyst prepared with tetraethyl ammonium hydroxide (TEAOH) had about one-half to two-thirds the activity of the 72 CAER coarse catalyst from which it was prepared; see Table 3 and Figures 2 and 6. The selectivity of CO conversion to the various hydrocarbons followed that of the parent catalyst; see Table 3 and Figure 10. In summary, this approach was not effective.

As shown in Figures 2 and 6, two of the catalysts prepared with CTABr (116A and 116C) exhibited activities and selectivities equivalent to the 77B catalyst. The 116B catalyst that was prepared in manner similar to that of 116A but with one-third of the SiO_2 precursor had much less activity than 116A. There is no obvious reason for this difference in activity.

Additional CTABr catalysts (134A and 135A) were prepared with different levels of SiO_2 precursors and reactants to determine if a fibrous/fractal or porous coating could be achieved and yet be catalytically active. Samples of these catalysts were calcined at temperatures of 400°C, 475°C, and 550°C. The results are given in Table 5 and Figures 3 and 7.

The 135A catalyst that had been calcined at 550°C (135A/550) exhibited activity about equal to that of 72 CAER catalyst. The 135A/475 catalyst was almost as active, and 135A/440 was about 20% less active. Therefore, coating iron oxide FT catalyst using the CTABr procedure and a low level of SiO_2 is not detrimental; however, calcination with relatively high temperatures appears to be necessary. As shown in Figures 6 and 7, the selectivity of converting CO to hydrocarbons alone (as opposed to CO_2 plus hydrocarbons) was reduced with the coating of FT catalysts with SiO_2. Therefore, the overall procedure was not as effective as desired.

The distributions of hydrocarbons generated with the various catalysts were similar, as shown in Figures 10 and 11. The peak occurred at a carbon number of C_3 to C_4 (propane and butanes). Low yields of ethane and ethylene were not expected, considering the typical product distributions from FT processes. The GC calibrations were checked and found to be valid; however, it was outside of the objective of this project to test this aspect further.

d. SiO_2-Surface-Coated CAER Catalysts Using Acidic Precipitation Techniques

As reported by Brinker et al.,[10] Brinker and Scherer,[11] and Klein,[12] silica that is acid-catalyzed in an alcohol solvent system with only a low level of water forms a fractal structure that is somewhat linear with an open structure. Base-catalyzed silica is more highly cross-linked and brittle. The structure of the gel is highly dependent upon the SiO_2 precursor (typically tetraethylorthosilicate [TEOS]), water level, pH (acid or base concentration), temperature, aging/curing time, and subsequent calcination conditions. As noted in Chapter 1 of Brinker et al.,[10] acid-catalyzed gels with low water addition were clear and rubbery, which was consistent with a weekly cross-linked system. Base-catalyzed gels were often brittle and cloudy, indicating a highly cross-linked system.

Consistent with the above literature, one series of experiments was made with H_2SO_4 at a pH of about 2.0 and low feed concentration of water in ethanol. H_2SO_4 was used in an attempt to avoid catalyst containing Cl that may be corrosive to stainless steel reactors. A second series then was

made with HCl, because H_2SO_4 generated catalysts with low activity. A third series was made with HNO_3. Summaries of the catalyst preparations and FT experiments are given in Tables 1 and 2. The results of the acid-catalyzed catalysts are given in Figures 4 through 9 and Tables 6 through 8.

As shown in Figure 4 for the H_2SO_4-precipitated catalysts, only catalyst 178D was as active as the coarse CAER FT catalyst in the conversion of CO. This 178D result is unusual in that this catalyst contained the highest level of SiO_2. The remaining SiO_2-containing catalysts (178A, 178B, and 178C) exhibited very low activity levels. Even the reference catalyst (180A), which was made without TEOS but with the acid treatment step, had a very low activity level. Apparently the presence of sulfate radicals was detrimental to the reactivity of iron-containing FT catalysts. No further testing of this system could be justified.

As shown in Figures 5 and 9, the activity of the lowest SiO_2-containing catalyst (183A) made with HCl treatment was about equal to that of the coarse CAER catalyst. The charge level of TEOS in this case was 0.114 g TEOS per 1.50 g CAER FT catalyst; this is equivalent to 0.022 g SiO_2 per gram of catalyst (i.e., 2.2%). When the charge level of TEOS was doubled (183B) and quadrupled (183C), the resulting catalyst activity level was reduced to about one-half. Therefore, the surfaces of the later two catalysts were being blocked. As noted in Figure 12 and referring to Figure 11, the distribution of hydrocarbon products was similar to those of the previous base-treated catalysts.

A series of SiO_2-containing catalysts (30AA through 30CC) was made using HNO_3 to precipitate SiO_2 prior to mixing with CAER catalyst. As shown in Figures 5 and 9, the first two catalysts (30AA and 30BB) were at least as active as the coarse CAER catalyst. The third catalyst (30CC) was about two-thirds as active.

The most active catalyst (30AA) for CO conversion was prepared in a step-wise procedure to generate fractal SiO_2 precipitate prior to being contacted with the CAER catalyst. Specifically, TEOS (0.23 g SiO_2 per gram of catalyst) was mixed with ethanol and contacted with a dilute HNO_3 ethanol solution with a low level of water present (note Table 1 for the specific amounts). SiO_2 was allowed to form at 25°C for 24 hr and cure at 45°C for 48 hr prior to the addition of 1.50 g CAER catalyst. The catalyst slurry was held at 45°C for four additional days, and then it was recovered and calcined at 500°C. Catalyst 30BB was prepared using the same charge weights as 30AA, but the CAER catalyst was added after the first 24-hr period. The slurry was cured at 45°C for 48 hr prior to recovery and calcination. Catalyst 30CC was prepared in the same manner as 30BB, but the charge of TEOS was essentially doubled.

Even though 30AA was the most active catalyst of the HNO_3 series, its conversion level of CO to hydrocarbons (Figure 9) was the same as that of 30BB. This was due to a high level of CO_2 formation with 30AA (note also Figure 12). The increased level of SiO_2 coating with catalyst 30CC resulted in a decrease of FT activity.

In summary, the use of HNO_3 to form a SiO_2 surface coating on CAER FT catalyst was superior to HCl and H_2SO_4 acids and also the NH_4OH base for SiO_2 precipitation. In all of these cases, there was a decrease of FT catalytic activity that increased as the amount of SiO_2 increased. The best SiO_2 level was about 2.0–2.5 wt%. Considering the level of funding involved with this aspect of the project, no arrangements have been made to test particle strength here at Argonne National

Laboratory. However, as originally proposed, these results will be discussed with Dr. B. H. Davis of CAER.

Scanning Electron Microscopy (Physical Appearance and Catalyst Composition)

Field emission scanning electron microscopy (FE-SEM) was used to observe and analyze as-received and the above-treated FT catalysts. The instrument was a Hitachi S-4700 configured for SEM and energy-dispersive x-ray (EDX) spectroscopic analysis. Eight fresh and two used/recovered catalyst samples were scanned. Only a limited amount of sample was used, and there was no apparent cross-contamination between samples.

The first series of SEM scans was undertaken using raw and base-treated CAER catalyst samples. Eight fresh and two used/recovered catalyst samples were scanned as follows: (1) 132E, (2) 77B, (3) 134A/400, (4) 135A/400, (5) 135A/550, (6) 30AA, (7) Run 102 recovered catalyst made with as-received CAER catalyst, and (8) Run 153 recovered catalyst made with 135A/550 catalyst. The second series centered on samples of raw CAER catalyst and HNO_3 precipitated SiO_2 on the CAER catalyst (i.e., Runs 30AA and 30CC). The photomicrographs are included as Figures 13 through 37.

a. SEM Observations of Fresh Catalyst Samples (Series No. 1)

The FT catalyst solids were not uniform. The procedure of passing as-received CAER catalyst through four stages of differential sedimentation to recover a concentrate of large-size spherical particles was only partially successful. As shown in Figure 13, which was made with SEM 300X magnification, the as-received CAER catalyst recovered after differential sedimentation (132E) consisted of large (~50-70 μm) and small (~15-30 μm) spherical agglomerates and small chips. The SEM area shown in Figures 14 and 15 consisted primarily of smaller spheres and chips. The distribution of particles shown in Figure 16 (catalyst 135A/550) was similar to that shown in Figure 13. It appears that the large spheres were made up of agglomerates of particles. These small particles were, in turn, also agglomerates. The large spherical particles were reported by Davis[3] to have been formed as a result of spray drying. There were also a sizeable number of chips that were flint-like, with smooth surfaces and somewhat sharp corners. Apparently these chips were formed by the fracturing of the iron oxide/silica FT catalyst particles in that their Fe/Si composition was about the same as that of the overall catalyst, as discussed below. In confirmation, similar characteristics were observed in scans of spherical particles that had been crushed intentionally. There were also a limited number of almost pure iron chips that may have been contaminants.

5.0K Magnification: At 5.0K magnification, all of the large particles appeared to be an agglomeration of Aflaky@ material. These flakes were about 0.2 to 1 μm in length. Figure 17 includes four particles of Acoarse@ 132E CAER catalyst. Both the large (15 μm) and small (4 μm) particles were representative of typical spherical catalyst. The upper large sphere of this figure had a surface indicating some loss due to chipping of flakes. A typical flake also is included in this figure. Figure 18 is typical of a 132E catalyst particle that had been crushed. Figure 19 includes a combination of crazed spheres and chips of 135A/400 catalyst. The scan of 135A/550 (Figure 20) was more like that of the feed CAER catalyst with less crazing. Figure 21 is a scan of 77B, which contained the highest added level of SiO_2. There appears to be an increased amount of material adhering to the particle surface.

13K Magnification: An examination of the SEM 13K magnification scans again points out that the CAER base catalyst consisted of an agglomerate of flake-like solids. The scans of 132E, 134A, and 135A samples are similar (Figures 22 – 24). It appears that sample 77B has a heavy coating that has crazed with relatively deep cracks (Figure 25).

150K Magnification: All of the catalyst particles had a bumpy appearance, indicating that the CAER catalyst was formed by the agglomeration of small (~150 nm) sub-particles that were, in turn, also agglomerates — presumably colloidal iron oxide. The 132E catalyst surfaces appeared to be rougher than the other catalyst surfaces (see Figures 26–29). The 77B surface (Figure 30) was somewhat smooth with what may have been a SiO_2 coating. However, this observation was made with only a limited number of samples.

b. SEM Observations of Used and Recovered Catalyst Samples

Two samples were examined after they had been recovered from the FT reactor; namely, catalysts from Run 102 made with as-received CAER catalyst and Run 153 made with 135A/550 catalyst. The recovered catalyst appeared to stick together in string-like groups. The particles were strongly magnetic, which was likely due to a high content of Fe_3O_4. The appearance of the recovered particles was similar to that of the raw catalyst with the exception that there were numerous small (0.1-0.5 μm) surface particles. See Figures 31 and 32 made at 13K magnification and Figure 33 made at 150K.

c. EDX Analyses of Fresh Catalyst Samples

Selected surfaces were analyzed using the energy dispersive x-ray (EDX) spectroscopy system. However, there were only a limited number of scans; no quantitative reference samples were available as references, and the beam penetrated through the surface. Therefore, the following are only semi-quantative observations about surface compositions:

1. Large particles of rough/raw CAER catalyst (132E) had an average surface Fe/Si atomic ratio of about 16.7, while that of a smooth fractured surface was higher at about 21.5. This observation is consistent with the proposition that Si was carried toward the surface during the spray-drying process. (The as-received CAER catalyst had an atomic Fe/Si ratio of 21.7.)

2. Large, rough 134A catalyst particles had an average surface Fe/Si ratio of about 9.7, while that having a smooth surface was higher at about 18.3.

3. Large, rough 135A/400 catalyst particles had an average surface Fe/Si ratio of about 13.8, which was about equal to that of 135A/550 catalyst, which averaged 12.9. A smooth surface on a chip was higher at about 25.4. There was also a chip-like particle that appeared to be iron alone, namely, a Fe/Si ratio in excess of 400.

The relative order of the Fe/Si atomic ratios of the above three catalyst samples is consistent with expected Si levels. The 132E is an untreated CAER catalyst prepared with about 5% SiO_2; additional SiO_2 was added in the preparation of 134A, and about one-half of the added SiO_2 of 134A was used in the preparation of 135A.

There was also a minor EDX peak attributed by the instrument to Co in all of the spectra. The atomic ratio of Fe/Co was 20 or greater when identified and reported. There is no explanation posed for this Co presence.

d. EDX Analyses of Used and Recovered Catalyst Samples

The EDX analysis of the surface of Run 153 recovered catalyst particles averaged a Fe/Si atomic ratio of 13.3, and that of a smooth surface was 16.7. These ratios are the same as those of the fresh catalyst. The observed C/Fe atomic ratio of the surface was high at about 6.6; again, note that reference calibration samples were not available to establish absolute levels. The observed C/Fe atomic ratio of a smooth particle surface was only 1.0, and that of fresh catalyst averaged 0.4. Therefore, there was only a limited penetration of carbon (i.e., CO) into the FT catalyst during conditioning and FT reaction steps. This observation also indicates that the FT reaction occurs near the surface of a Fe-based catalyst. By inference, broken pieces of catalyst would exhibit low catalytic activity, considering that it has been reported[6] that a FT catalyst is best conditioned with pure CO, as opposed to a H_2/CO blend, and the active FT surface is Fe_2C_5.

e. SEM Series 2

A short second series of SEM experiments was carried out using CAER FT catalyst onto which SiO_2 was precipitated using HNO_3. It was proposed that this acid would generate a fractal-like coating on the CAER catalyst, and we carried out these observations to determine if some effects or trends could be noted. Samples of raw catalyst and 30AA and 30CC were scanned at magnifications of 100X, 1K, 5K, 50K, and 200K. As shown in Figures 34 through 34, the scans started with a field of particles and then centered upon a single spherical particle with increasing magnification.

As shown in Figure 34, the low magnification (100X) scans were similar to each other and to those discussed above. Individual spherical particles were chosen at a magnification of about 1K; see Figure 35. These particles were spherical agglomerates of smaller agglomerates. Figure 36 presents the surface of the three catalyst particles taken at 50K. The surfaces of the SiO_2-coated particles (Figs. 36b and 36c) appeared to be rougher than that of the raw CAER catalyst. This observation appeared to be true on other areas of these particles.

In addition, elemental distributions were obtained using the above EDX technique. Typical average surface analyses are shown in Figure 37. Fe, Si, O, and C were identified. The following is a tabulation of the normalized quantification results (note that a reference standard was not used, so these results are estimates):

Sample	Raw CAER		30AA_CAER		30CC_CAER	
Element	Wt %	Atom %	Wt %	Atom %	Wt %	Atom %
C K	6.94	18.07	5.77	13.78	4.60	12.18
O K	20.88	40.82	28.47	51.04	22.73	45.17
Si K	1.21	1.34	2.76	2.82	2.28	2.58
Fe K	70.98	39.76	63.00	32.36	70.39	40.07

The table above confirms that additional SiO_2 has been deposited on the surface of 30AA and 30 CC. Because the SEM beam penetrated into the surface, a sizeable Fe signal was observed in all cases.

Compositional maps at 3K magnification were also prepared (Figures 38 and 39). There was a significant difference between the maps of the 30AA and 30CC catalysts. As noted above and in Table 1, catalyst 30AA was prepared by contacting the SiO_2 precursor (TEOS) with HNO_3 for 24 hr at 25°C and 48 hr at 45°C prior to the addition of the CAER FT catalyst. It was then aged for 48 hr. In the case of 30CC, the amount of TEOS was doubled, but there was only a 24-hr period of aging at 25°C prior to CAER addition and a subsequent 48-hr aging at 45°C. It is presumed that a more uniform coating along with penetration would be generated in the case of 30CC. As shown in Figures 38 and 39, this presumption appears to be valid based on the following observations:

1. Both catalyst surfaces are irregular, with the 30CC perhaps being a bit smoother than 30AA.
2. The concentration of Fe appears to be somewhat uniform in both catalysts (concentration is proportional to the lightness of the signal.) The Fe concentration is somewhat higher in the region of the cavity shown on the left side of 30AA.
3. There is a low concentration of Si and O in the cavity region of 30AA.
4. The concentrations of Si and O appear to be more uniform on the 30CC catalyst than 30AA, and they are less correlated with surface irregularities.

With additional SEM time and expense, it would be possible to expand upon these observations, including learning more about the depth and uniformity of Si penetration into the catalyst particles. It would also be necessary to use more realistic catalyst preparation times. Obviously, the long times involved with the above catalyst treatments were used to observe whether or not presumed fractal coatings were formed.

Cobalt-Containing Catalysts

A parallel series of exploratory experiments was undertaken using cobalt- and silica-containing precursors to determine the capability of preparing cage-like catalyst particles and observing their characteristics by SEM.

Under one of the procedures tested, nanocrystalline silica was impregnated with a transition metal salt ($Co(NO_3)_2$) and thermally treated under different environments. A combination of secondary electron (SE) and backscattered electron (BSE) images showed that silica nanocrystals rearranged around large metal oxide particles (~1 μm) in the case of high-metal-loaded samples that were air calcinated at 500°C. Subsequent treatment under reducing wet conditions and limited thermal treatment increases both the silica shell thickness and the size of the oxide particle (1-2 μm). The

nature of the oxides after the calcinations and reduction steps was identified as tricobalt tetroxide (Co_3O_4) and cobalt oxide (CoO). Non-calcined samples treated under the identical reducing conditions formed smaller cobalt oxide particles (100-300 nm) on top of large silica agglomerates. Reduced coating of the metal oxide particles by the silica nanocrystals was observed in this later case.

Summary of SEM Observations

The following points are noted:

1. Spherical particles of CAER FT catalyst were made up of agglomerates of particles that were, in turn, also agglomerates.
2. The coarse CAER catalyst characterization indicated that the spray-drying process apparently concentrated the Si precursor at the surface during drying.
3. SEM photomicrograph scans of raw and SiO_2-coated FT iron catalysts pointed out broad differences in the appearance of catalyst particles. With perhaps the exception of HNO_3-precipitated catalyst 30CC, there was little indication that the catalysts were being uniformly coated with a cage-like protective surface.
4. The surface Fe/Si atomic ratios of the catalyst samples were consistent with levels of Si used in their preparation.
5. There was only a limited penetration of carbon (i.e., CO) into the FT catalyst during the conditioning and FT reaction steps.

Interim Observations/Conclusions

The following interim observations/conclusions were drawn:

1. Iron-based catalysts can be prepared at Argonne using the techniques outlined in the CAER reports, but a high degree of mixing must be introduced to generate more uniform particle sizes. (The use of spray-drying catalyst particles should generate a more uniform distribution.)

2. The spray-dried bulk catalyst sample of CAER contains a high level of dispersed fine particles. A portion of these fines can be removed by differential settling techniques.

3. A flow unit with a fixed bed of diluted catalyst has been demonstrated for use in FT experimentation.

4. Reaction conditions have been established such that reasonable levels of CO conversion can be achieved with an active catalyst. These conditions can be used as a basis to compare catalyst samples.

5. SiO_2-coated iron-containing catalyst samples have been prepared using caustic precipitation techniques. A wide range of catalytic activities have been observed. As anticipated, the greatest activity was achieved with those catalysts coated with the least SiO_2. The activities of catalyst samples designated 135A/550 and 135A/475 were about equal to that of the

CAER coarse FT catalyst from which they were prepared.

6. In the case of the 135A series, calcination at 550°C and 475°C resulted in more active catalysts than that calcined at 400°C.

7. SiO_2-coated catalysts were prepared using acidic precipitation techniques; HNO_3 and HCl were effective while H_2SO_4 was not. The greatest FT activity was achieved with the catalyst having the least SiO_2 (i.e., 2.2 wt%).

8. SEM study indicated that the as-received CAER catalyst recovered after differential sedimentation (132E) consisted of large (~50-70 μm) and small (~15-30 μm) spherical agglomerates along with small chips. The catalyst particles recovered from FT runs had similar appearances. SEM, even at 150K magnification, did not appear to be an effective tool to differentiate various surface treatment procedures.

9. Large spherical particles were made up of agglomerates of particles that were, in turn, also agglomerates.

10. Chips had clean, smooth surfaces that had higher Fe/Si atomic ratios than those of the rough external surfaces, even in the case of the CAER as-received sample. The chips were the result of particle crushing, and they should represent the inside catalyst material. Therefore, the Si precursor was transported to the surface during the spray drying catalyst preparation process.

11. The relative order of the surface Fe/Si atomic ratios of the catalyst samples was consistent with levels of Si used in their preparation, so the EXD approach is reasonable.

12. The EDX Fe/Si ratio analyses of the surface of catalyst particles recovered after the FT reaction were the same as those of the fresh catalyst.

13. The C/Fe atomic ratio of the surface of a recovered FT catalyst particle was high at about 6.6, while that of a smooth particle chip was only 1.0 and that of fresh catalyst averaged 0.4. Therefore, there was only a limited penetration of carbon (i.e., CO) into the FT catalyst during conditioning.

Planned Experimentation

Considering that DOE requested that this program study iron-containing FT catalysts and that extensive literature has been published on the mechanisms, catalyst preconditioning, and product distributions of these catalysts, emphasis in this program centered upon the problem of formulating an attrition-resistant, yet catalytically active, iron-based catalyst. Experimentation has demonstrated that fractal SiO_2 can be coated upon FT catalysts with a minimum loss of activity. The results will be discussed with Dr. B. H. Davis of CAER to determine if further experimentation is warranted and if particle strength tests are justified.

Exploratory runs are being made using membranes with a novel technique to deposit active catalyst on surfaces. Results will be issued in subsequent reports.

Acknowledgements

This research was funded by the U.S. Department of Energy, National Energy Technology Laboratory.

Figure 1
Bench Scale Catalytic Unit

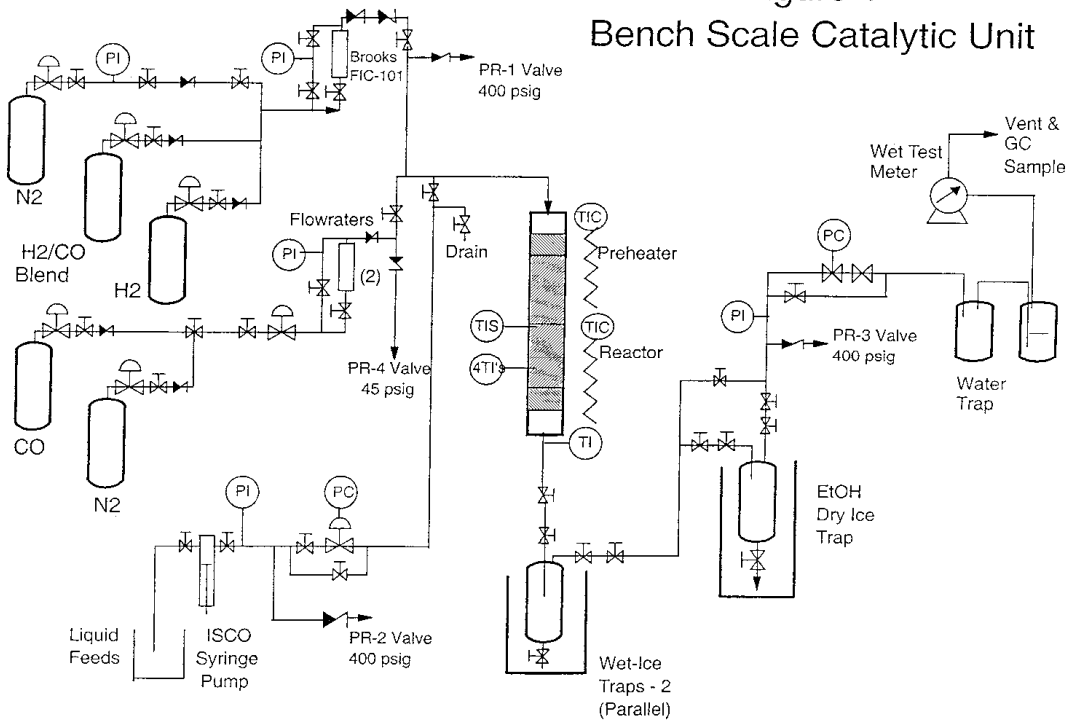


Figure 2. Conversion of CO Using AR CAER, 72Coarse, 77 and 116A, B & C Treated Catalyst

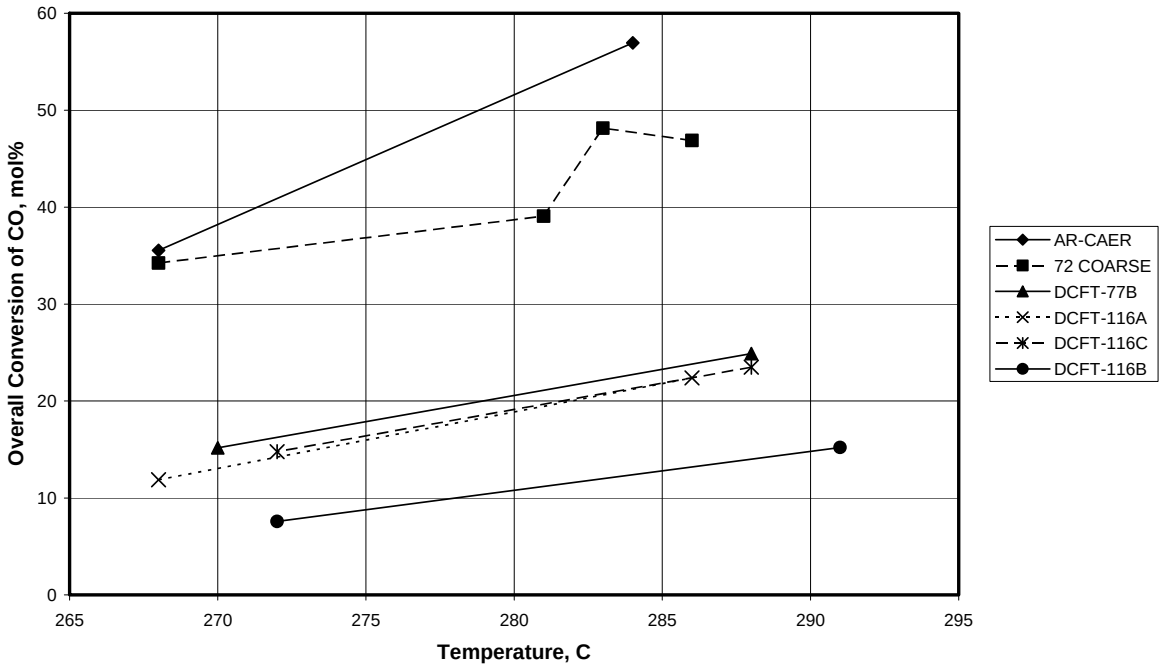


Figure 3. Conversion of CO Using 72Coarse, 116C, 134A(400&475), and 135A(400, 475 & 550) Treated Catalysts

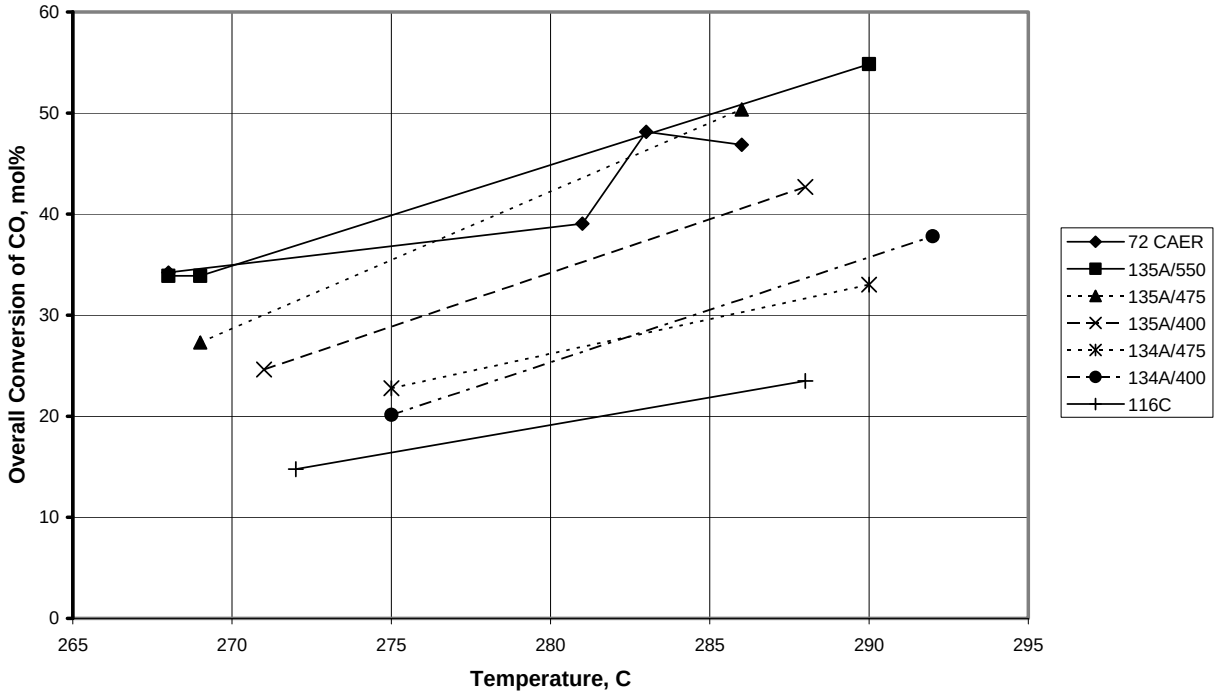


Figure 4. Conversion of CO Using 72Coarse, 180A, and 178A, B & C Treated Catalysts

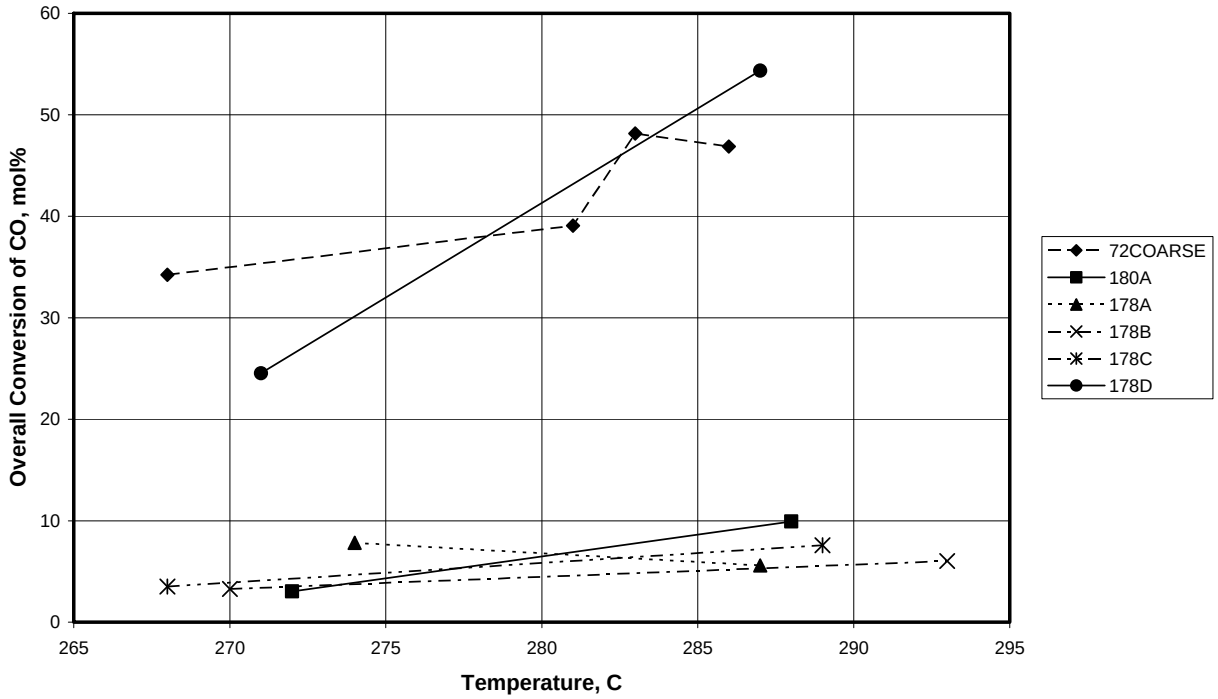


Figure 5. Conversion of CO Using 72Coarse, 183A, B, & C, and 30AA, BB & CC Treated Catalysts

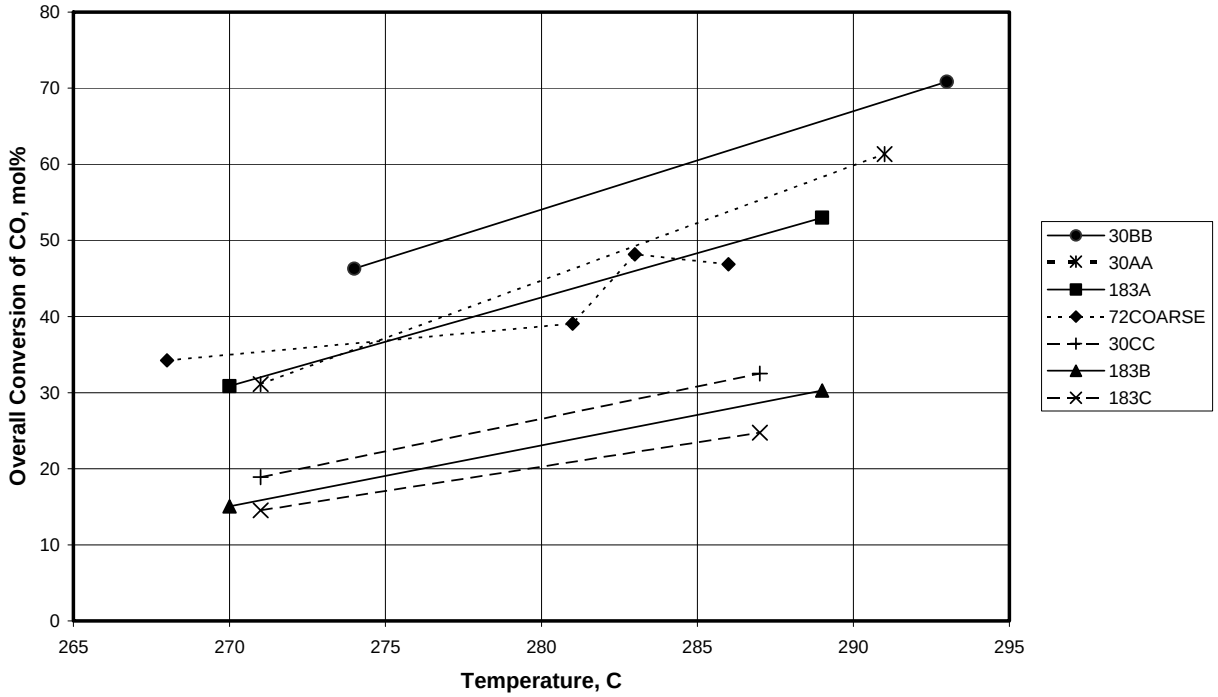


Figure 6. Conversion of CO to C1-C6+ Hydrocarbons Using AR CAER, 72Coarse, 77, 116A, B, and C Treated Catalyst

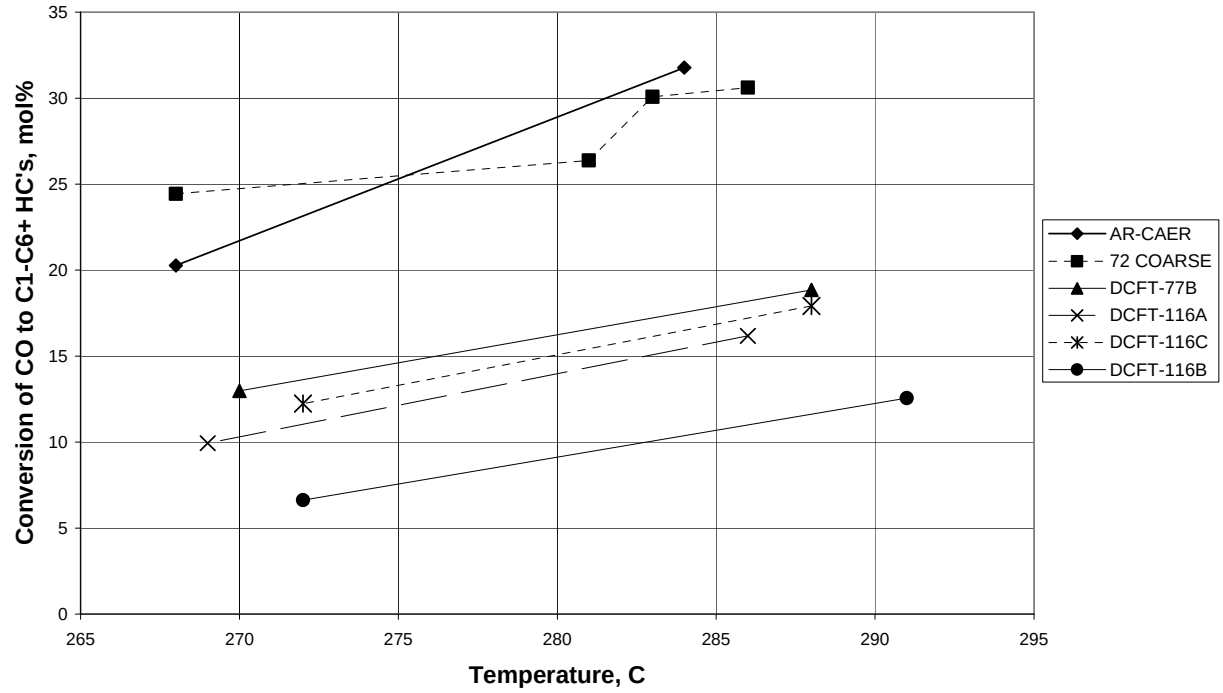


Figure 7. Conversion of CO to C1-C6+ HC's Using 72Coarse, 116C, 134A(400 & 475), & 135A(400, 475&550) Treated Catalyst

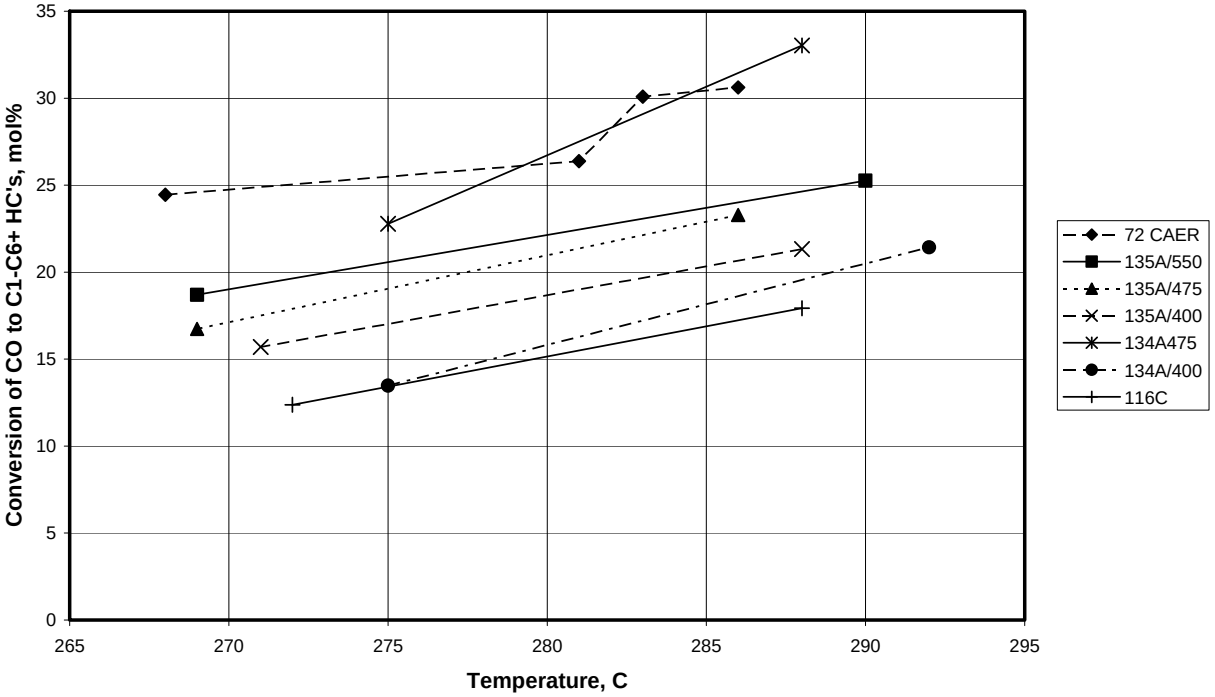


Figure 8. Conversion of CO to C1-C6+ HC's Using 72Coarse, 180A, 178A, B, & C Treated Catalysts

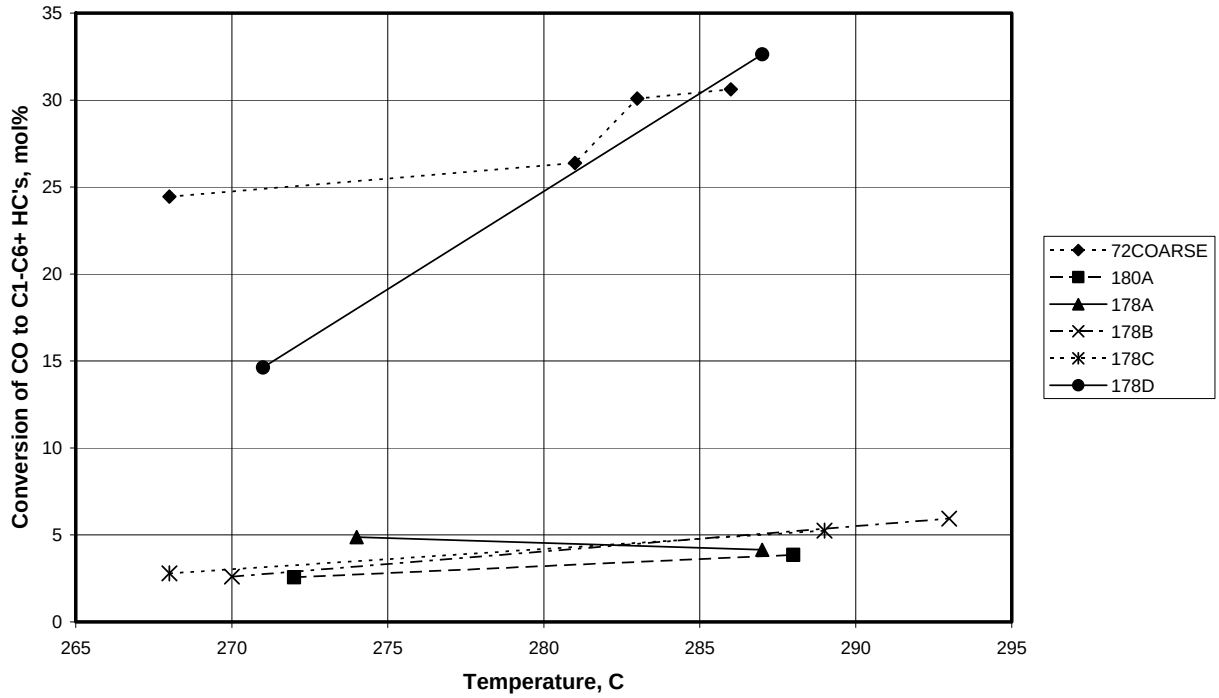


Figure 9. Conversion of CO to C1-C6+ HC's Using 72Coarse, 183A, B, & C, and 30AA, BB, & CC Treated Catalysts

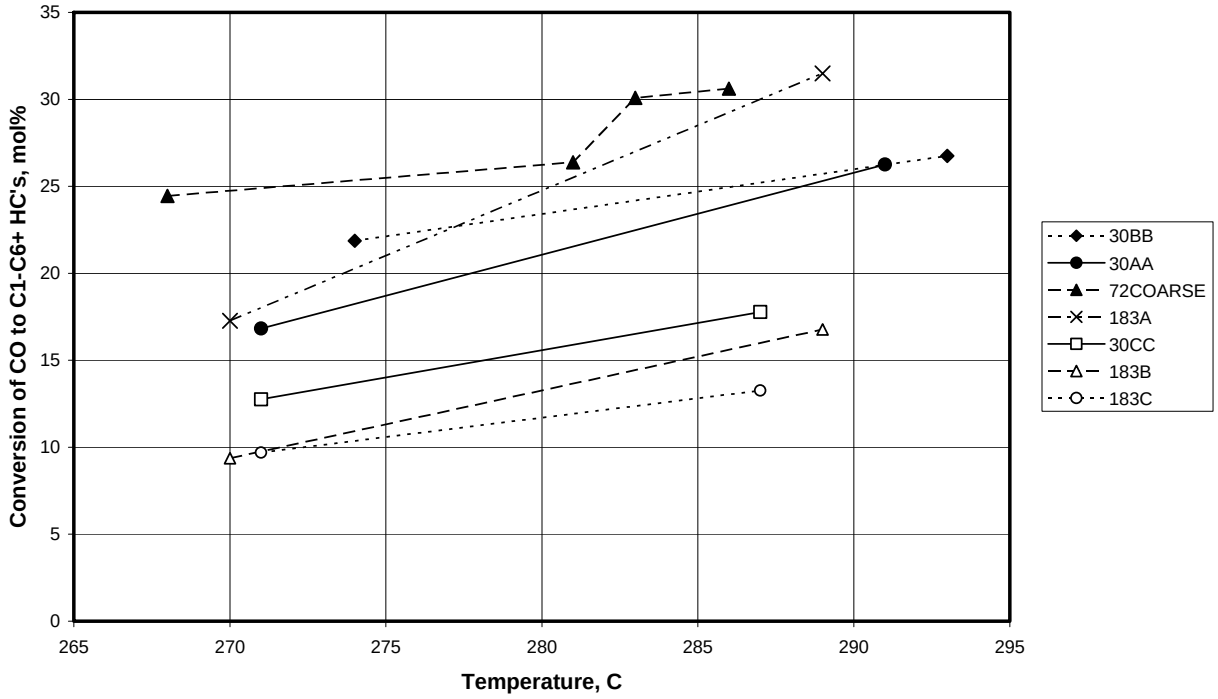


Figure 10. Selectivity at a Bed Temperature of About 285C Using AR CAER, 72 Coarse, 77 & 116 A, B, & C Treated Catalyst

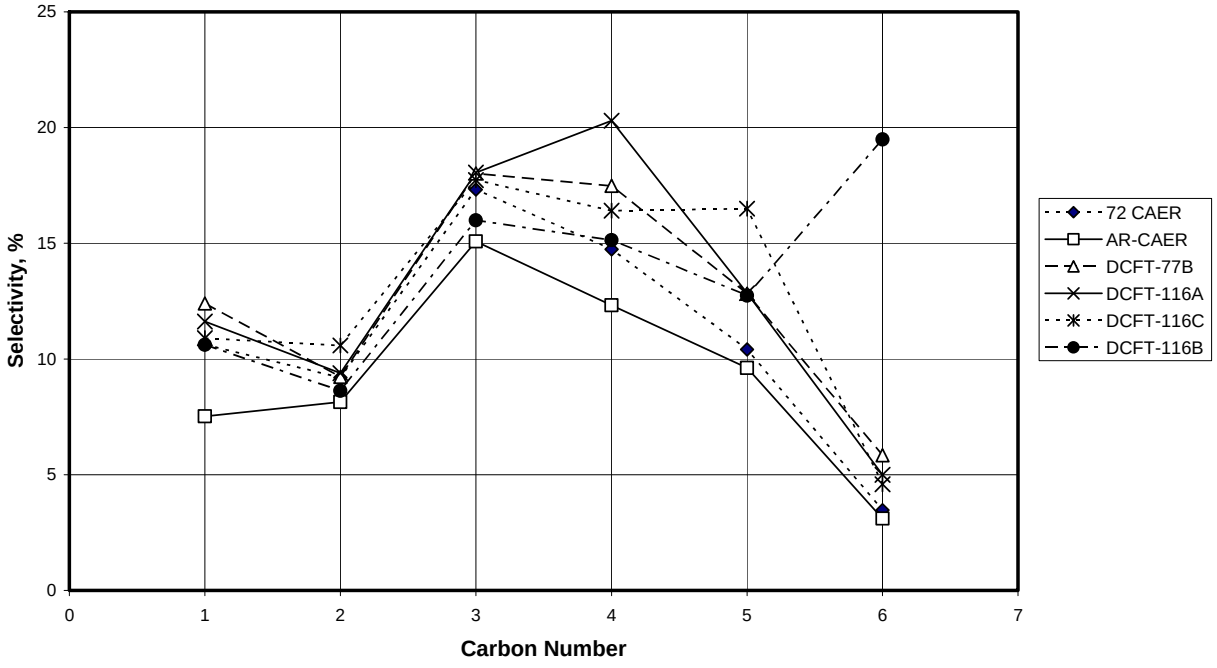


Figure 11. Selectivity at a Bed Temperature of About 285C Using 72Coarse, 134A and 135A Catalyst Calcined at 400, 475 and 550C

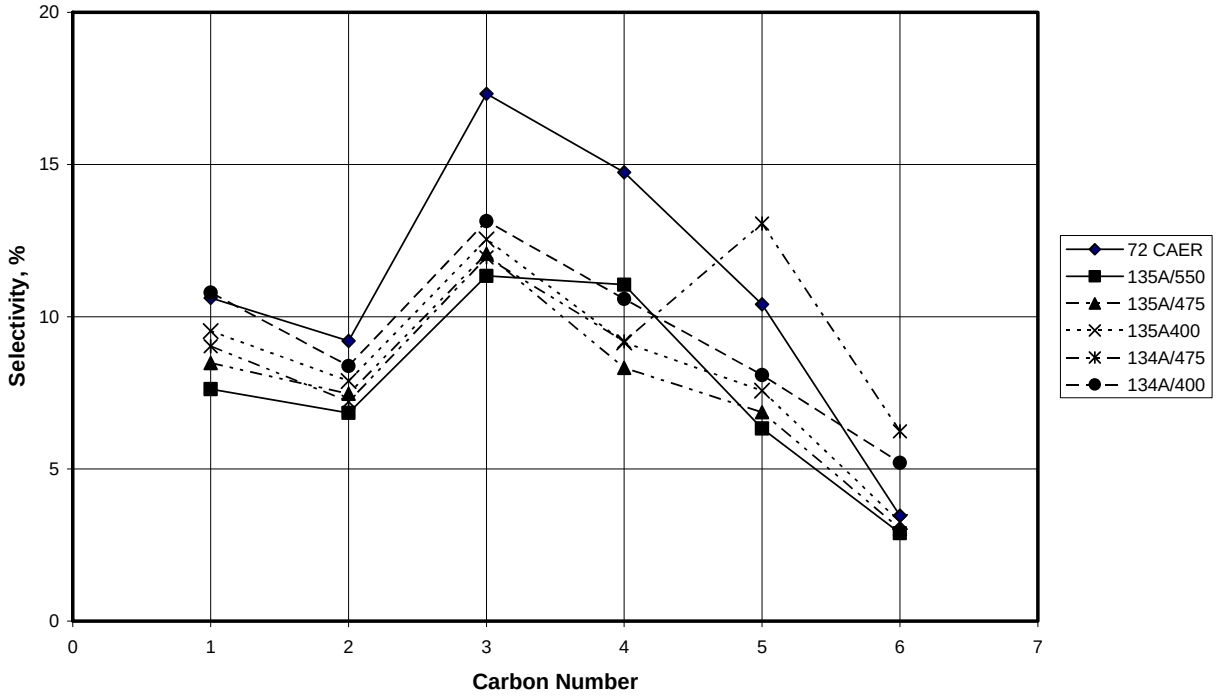
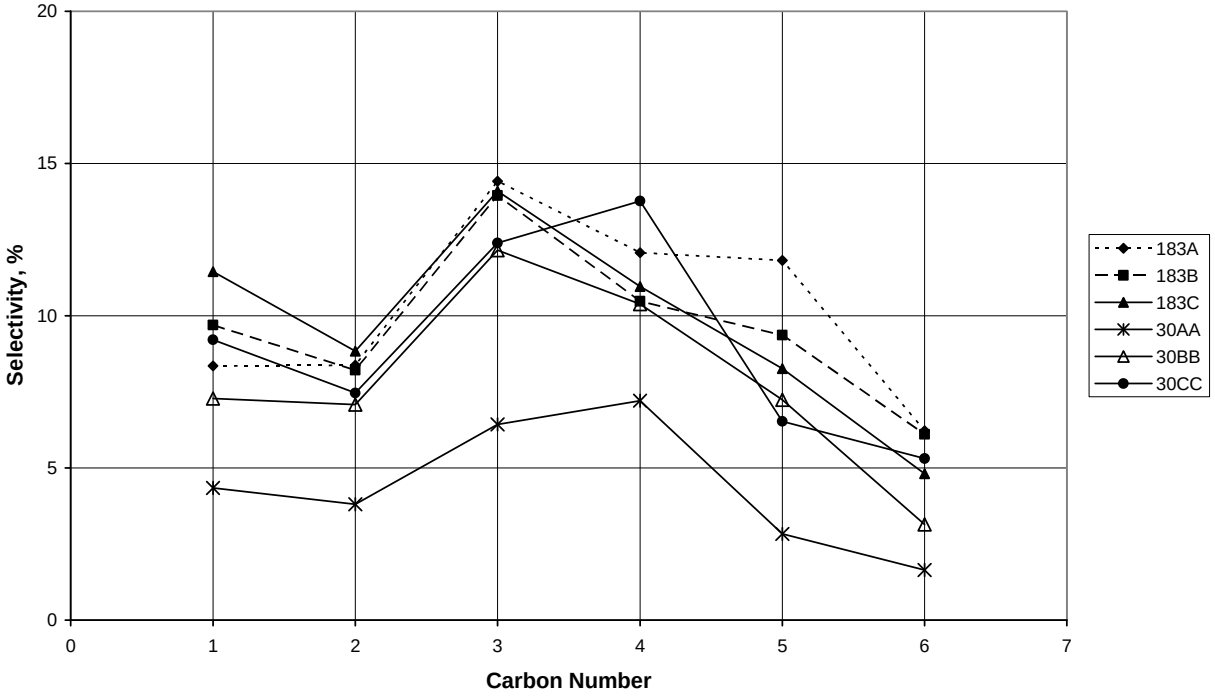


Figure 12. Selectivity at a Bed Temperature of About 288C Using 183A, B, & C, and 30AA, BB, & CC Treated Catalyst



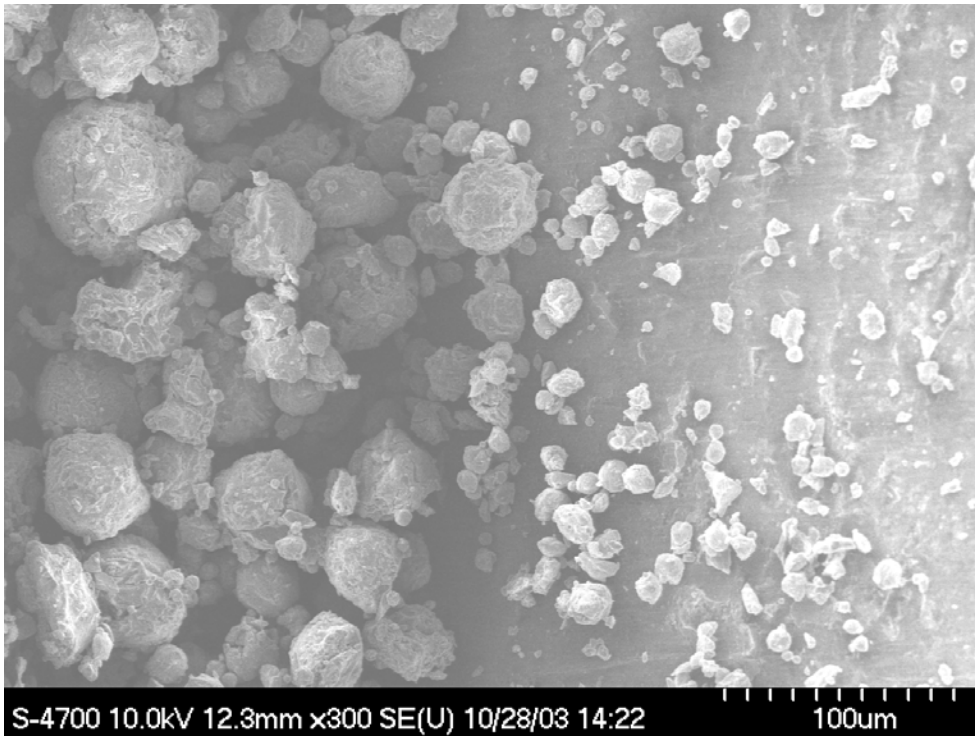


Figure 13. SEM 300X Magnification of CAER F-T Coarse Catalyst 132E

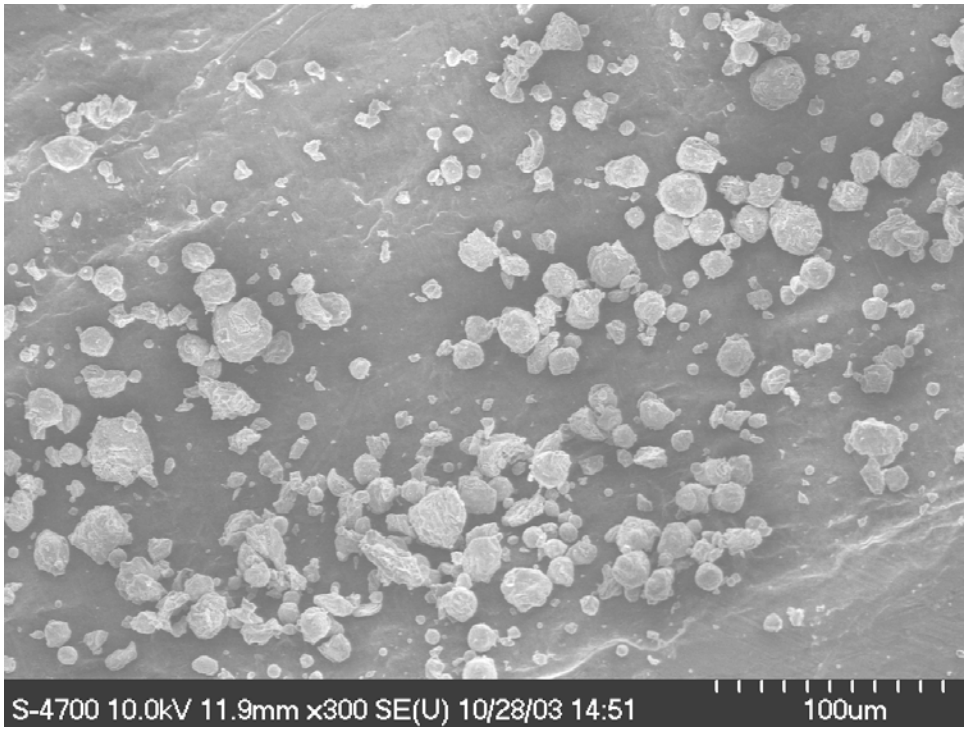


Figure 14. SEM 300X Magnification of Catalyst 134A/400

Figure 15. SEM 300X Magnification of Catalyst 135A/400

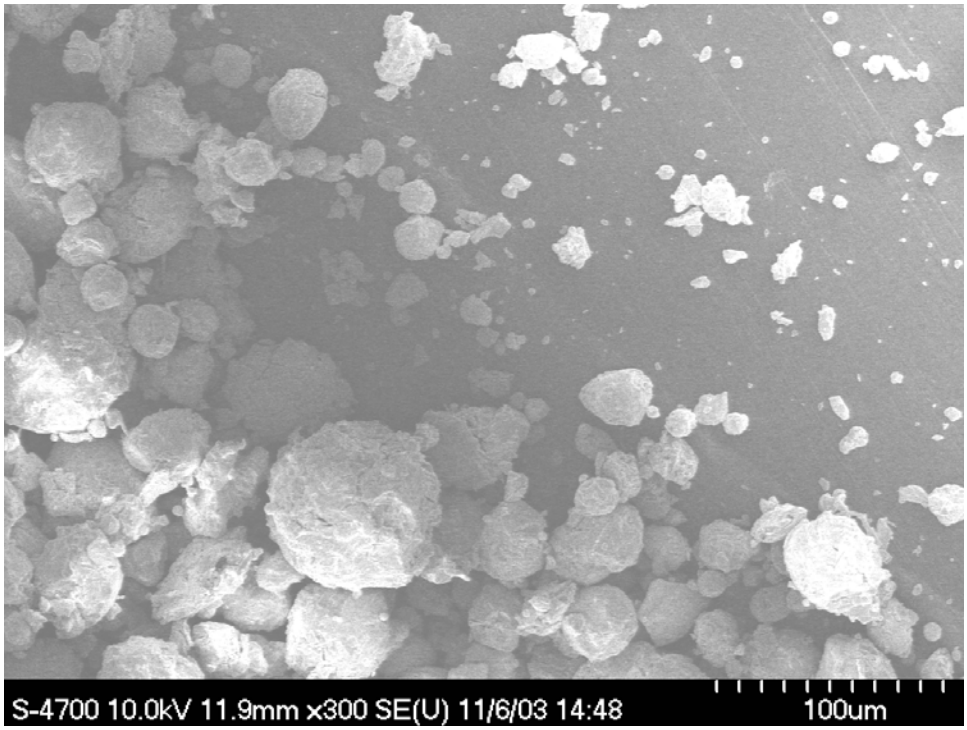


Figure 16. SEM 300X Magnification of Catalyst 135A/550

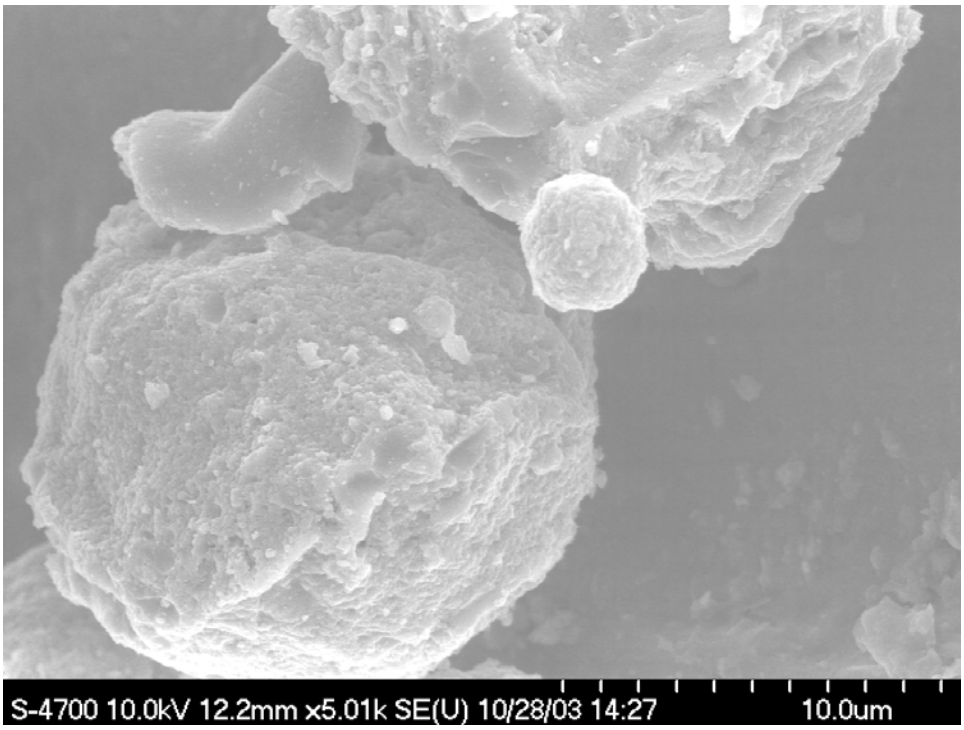


Figure 17. SEM 5 k X Magnification of Catalyst 132E

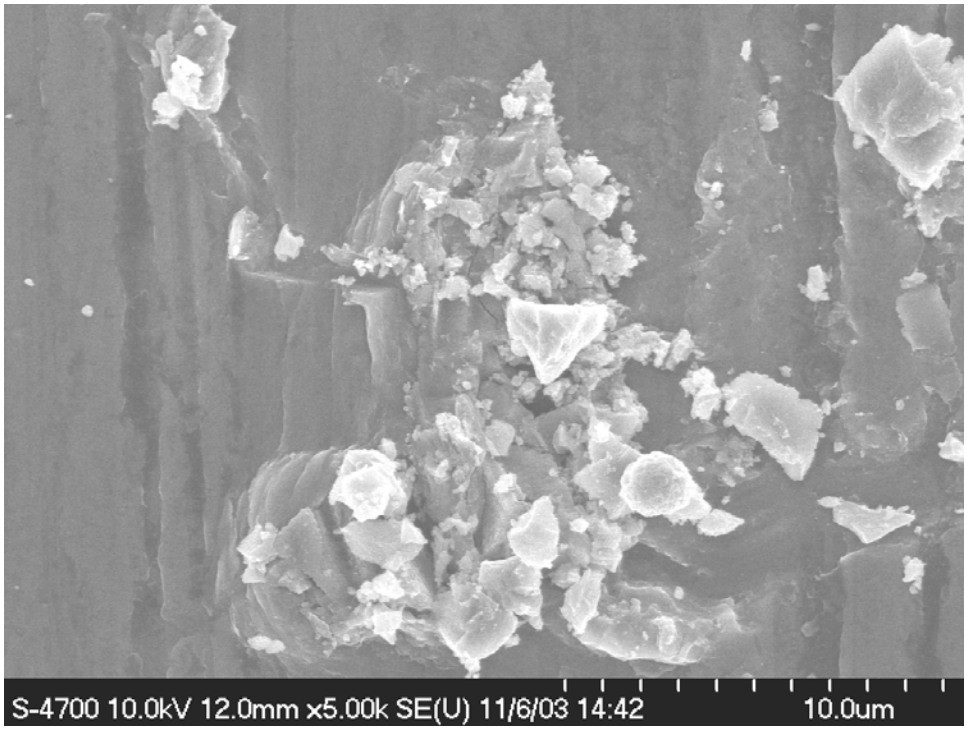


Figure 18. SEM 5 k X Magnification of a Crushed Sample of Catalyst 132E

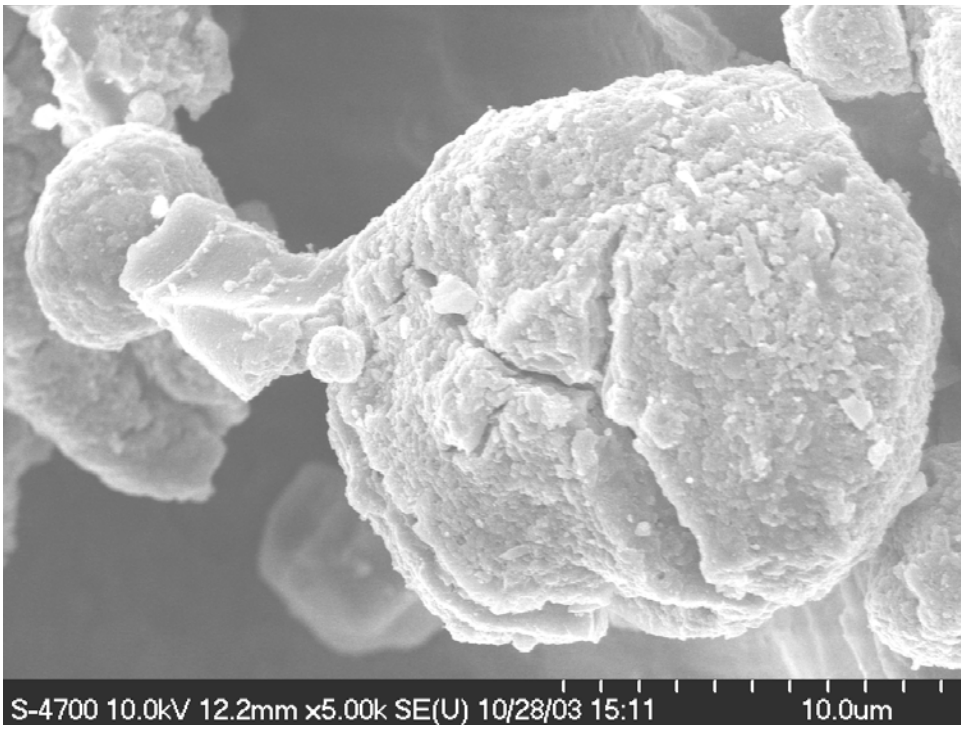


Figure 19. SEM 5 k X Magnification of Catalyst 135A/400

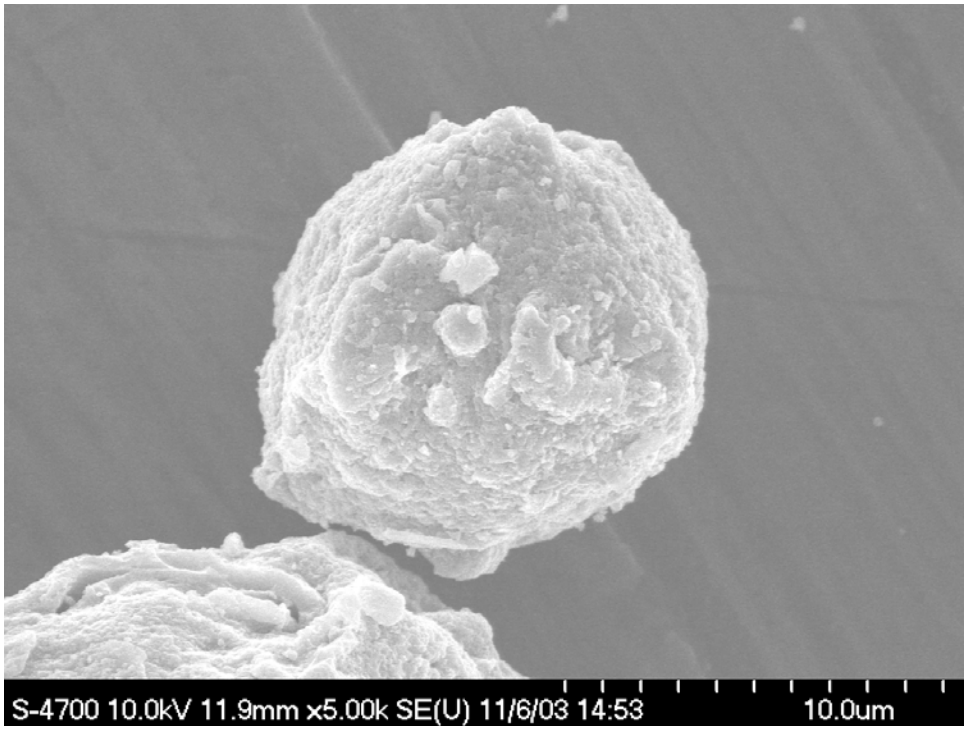


Figure 20. SEM 5 k X Magnification of Catalyst 135A/550

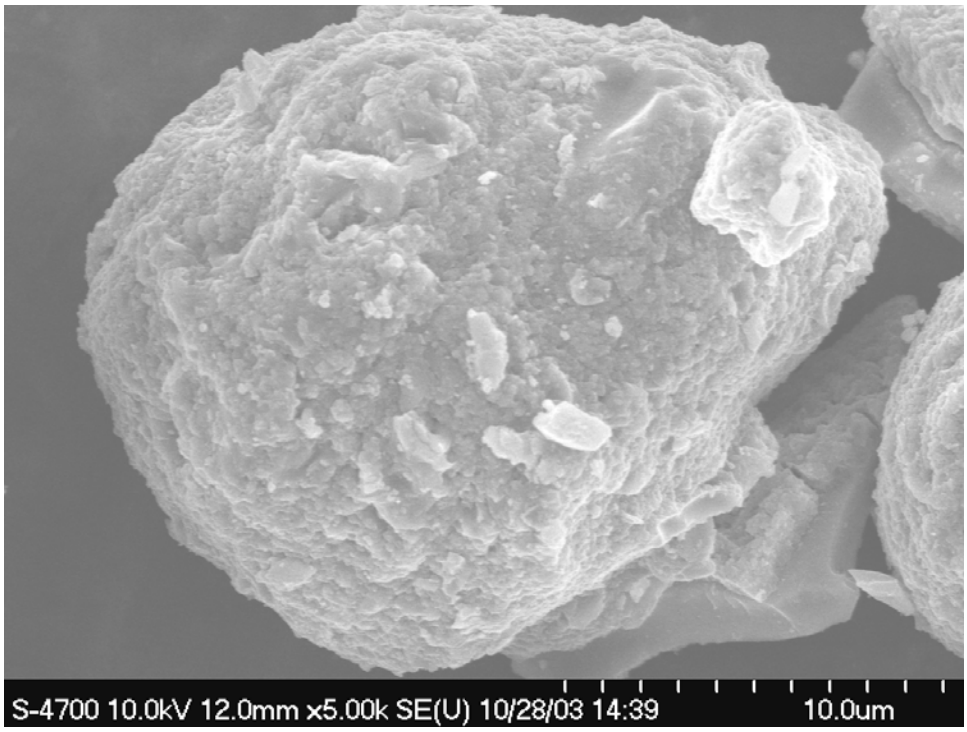


Figure 21. SEM 5 k X Magnification of Catalyst 77B

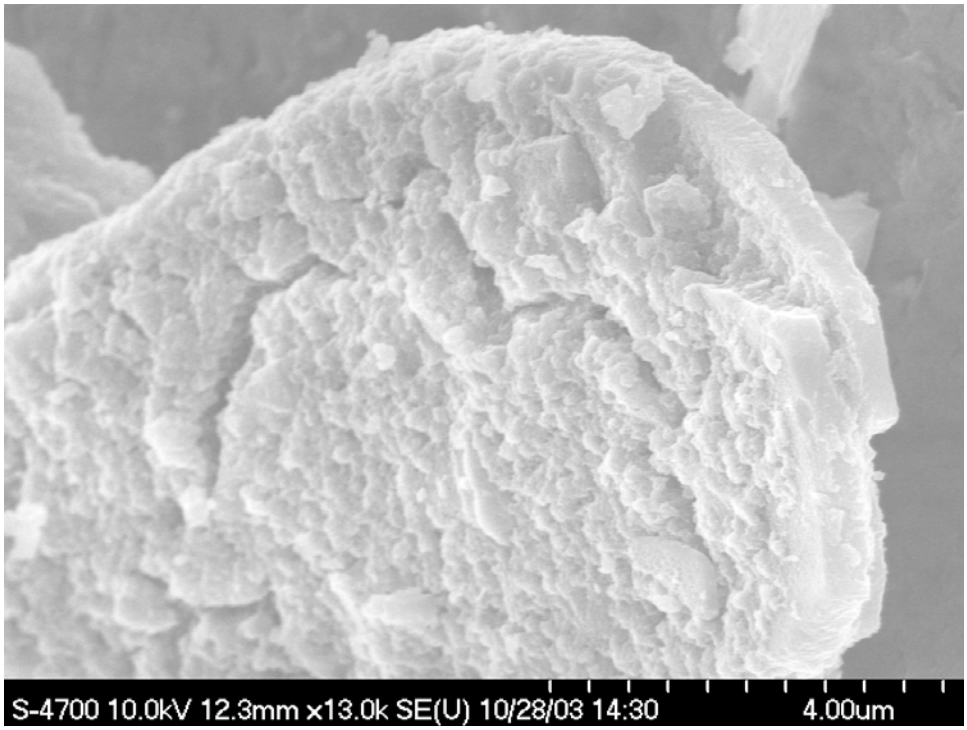


Figure 22. SEM 13 k X Magnification of Catalyst 132E

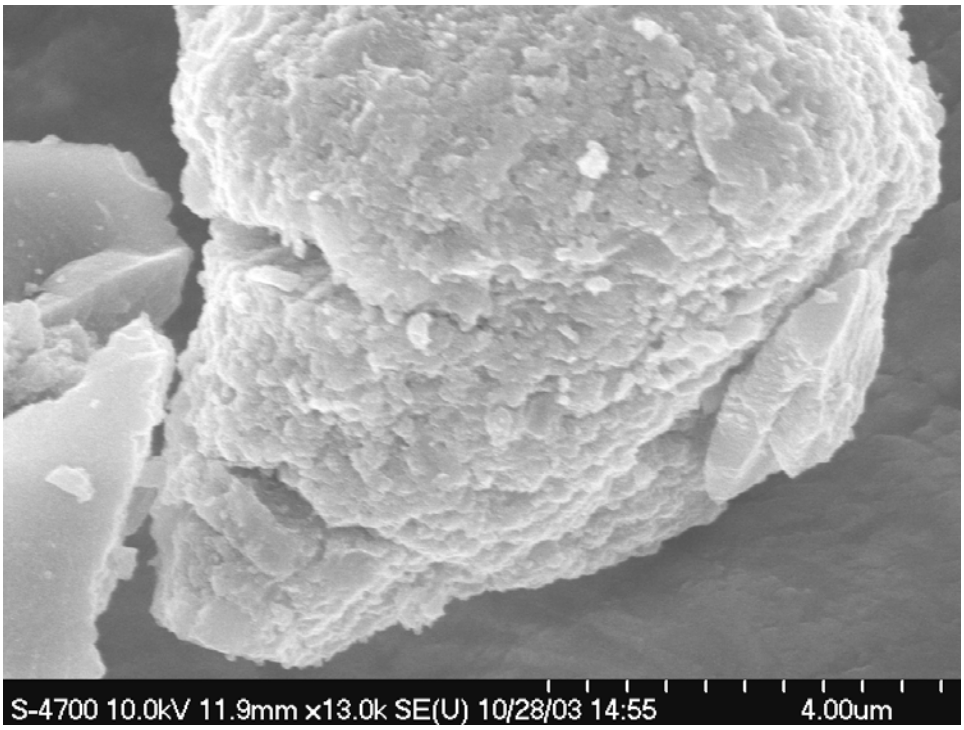


Figure 23. SEM 13 k X Magnification of Catalyst 134A/400

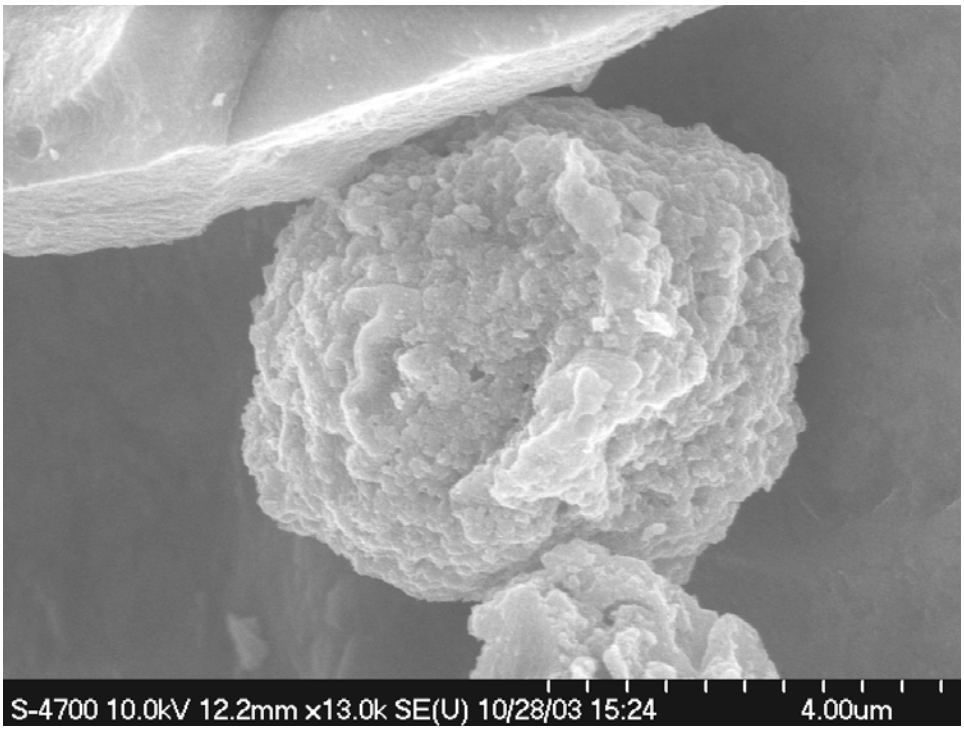


Figure 24. SEM 13 k X Magnification of Catalyst 135A/400

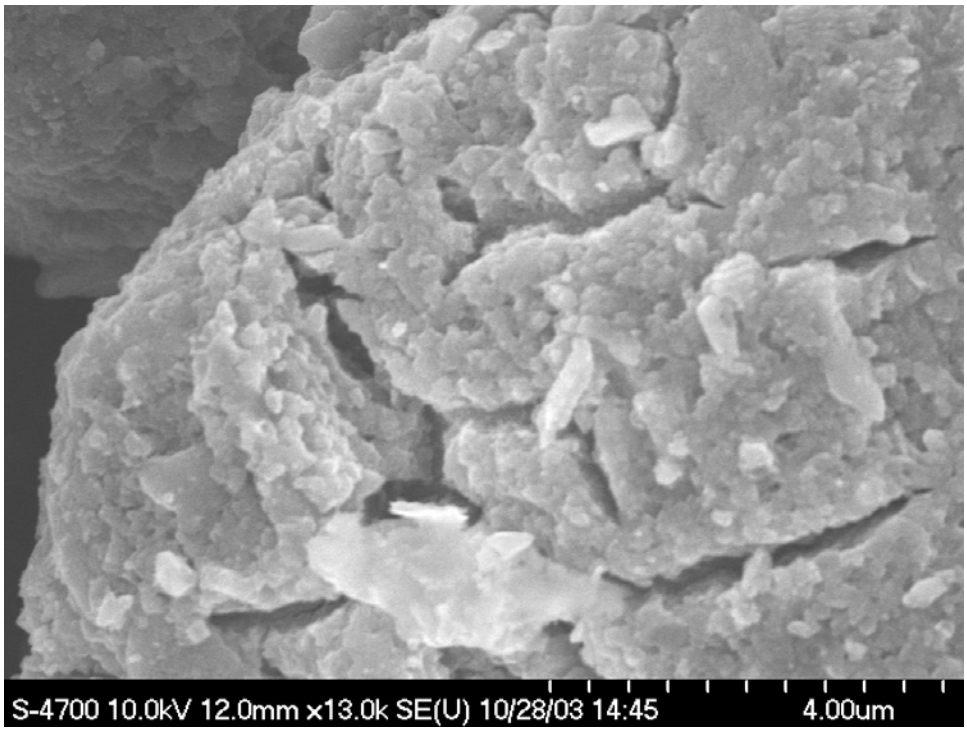


Figure 25. SEM 13 k X Magnification of Catalyst 77B

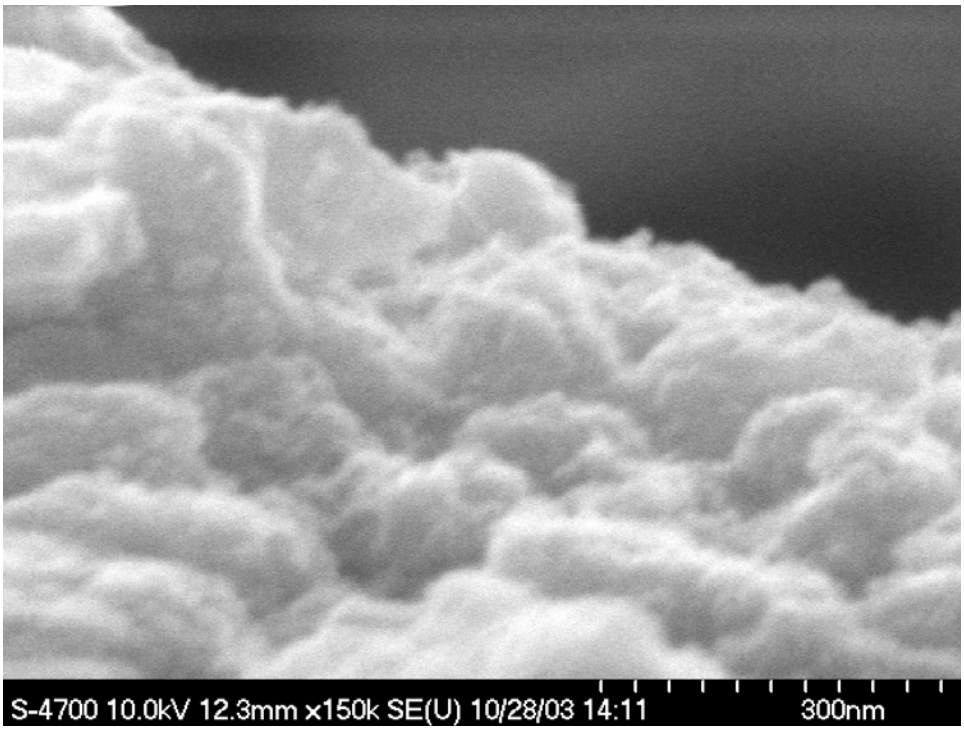


Figure 26. SEM 150 k X Magnification of Catalyst 132E

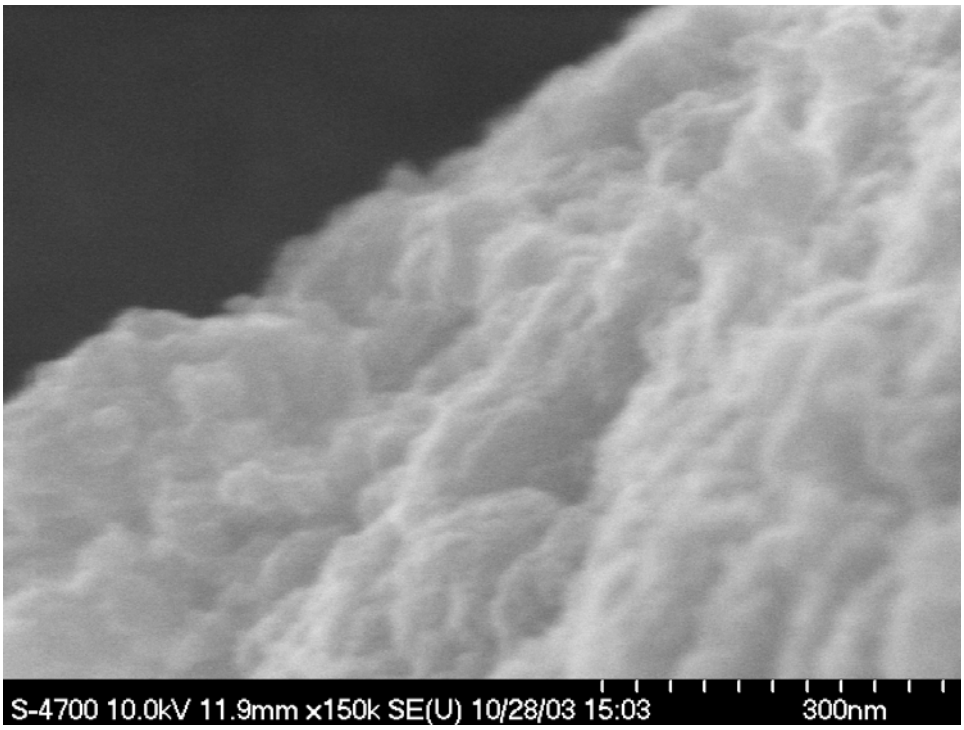


Figure 27. SEM 150 k X Magnification of Catalyst 134A/400

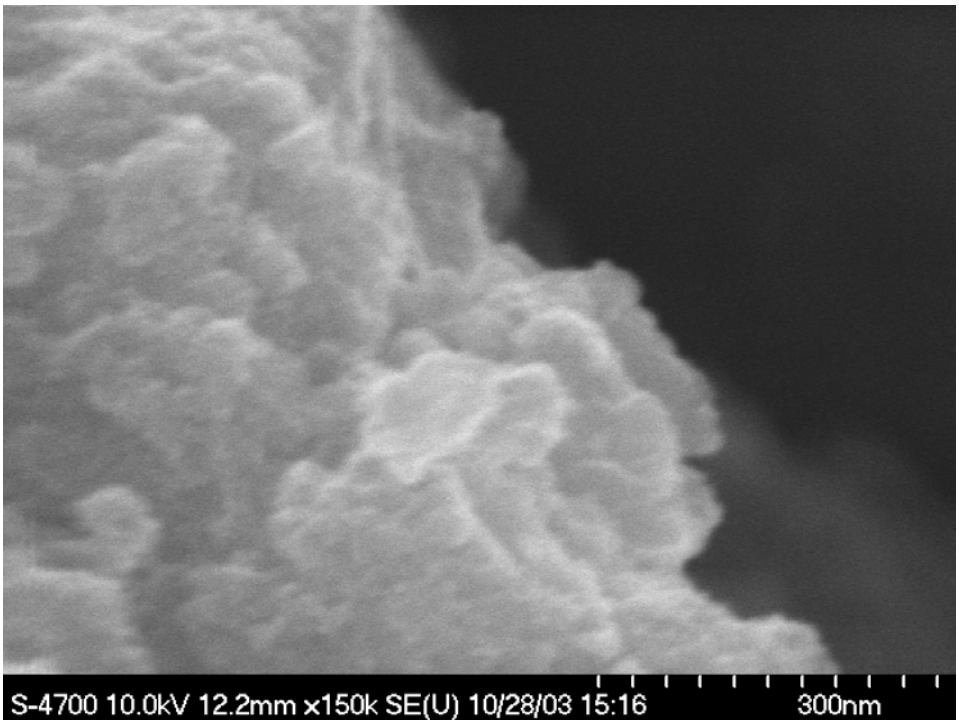


Figure 28. SEM 150 k X Magnification of Catalyst 135A/400

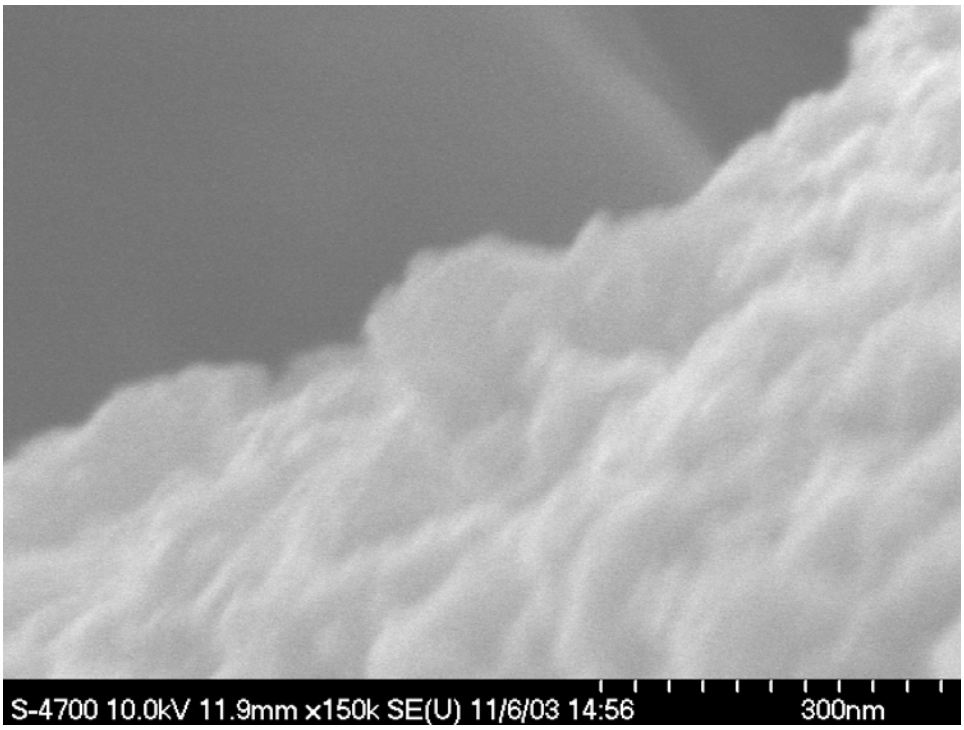


Figure 29. SEM 150 k X Magnification of Catalyst 135A/550

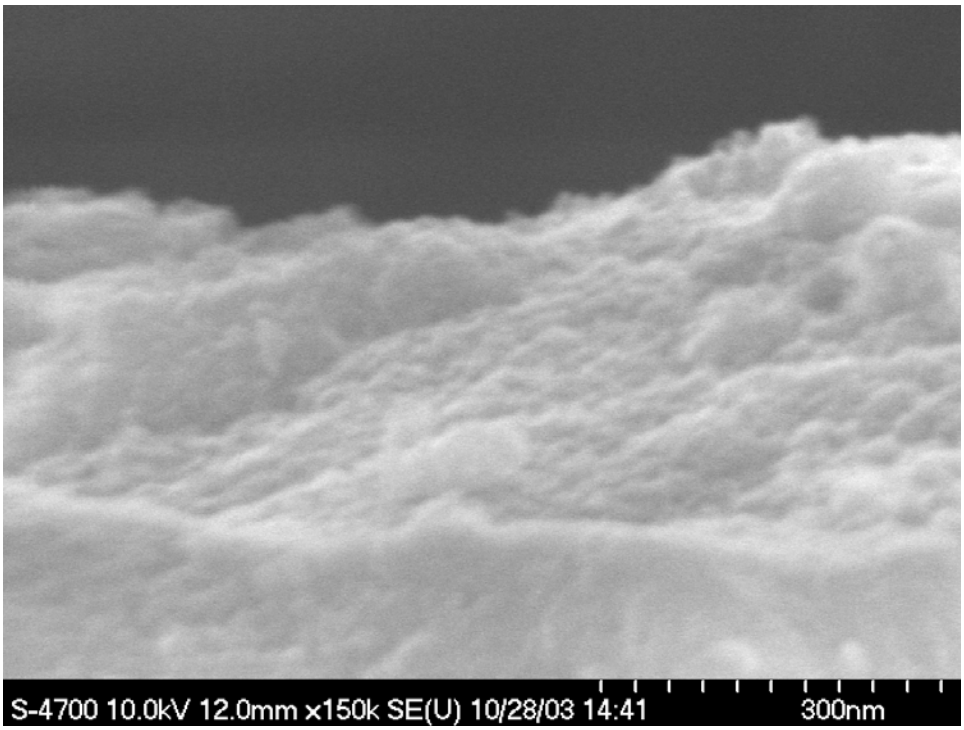


Figure 30. SEM 150 k X Magnification of Catalyst 77B/400

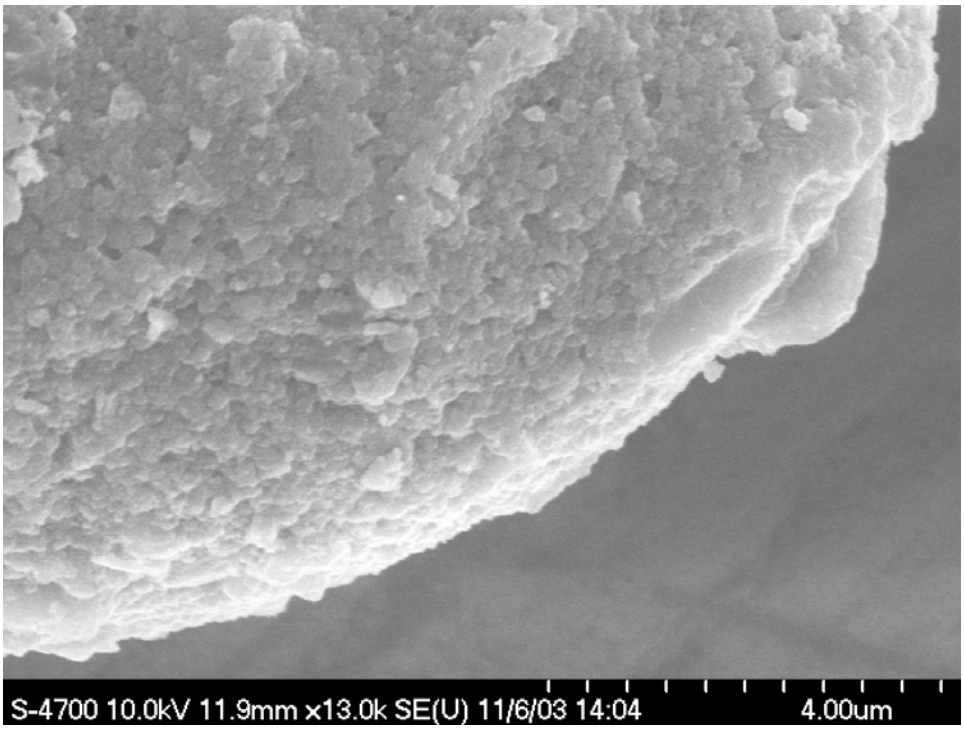


Figure 31. SEM 13 k X Magnification of a Round Particle of Recovered Catalyst of Run102

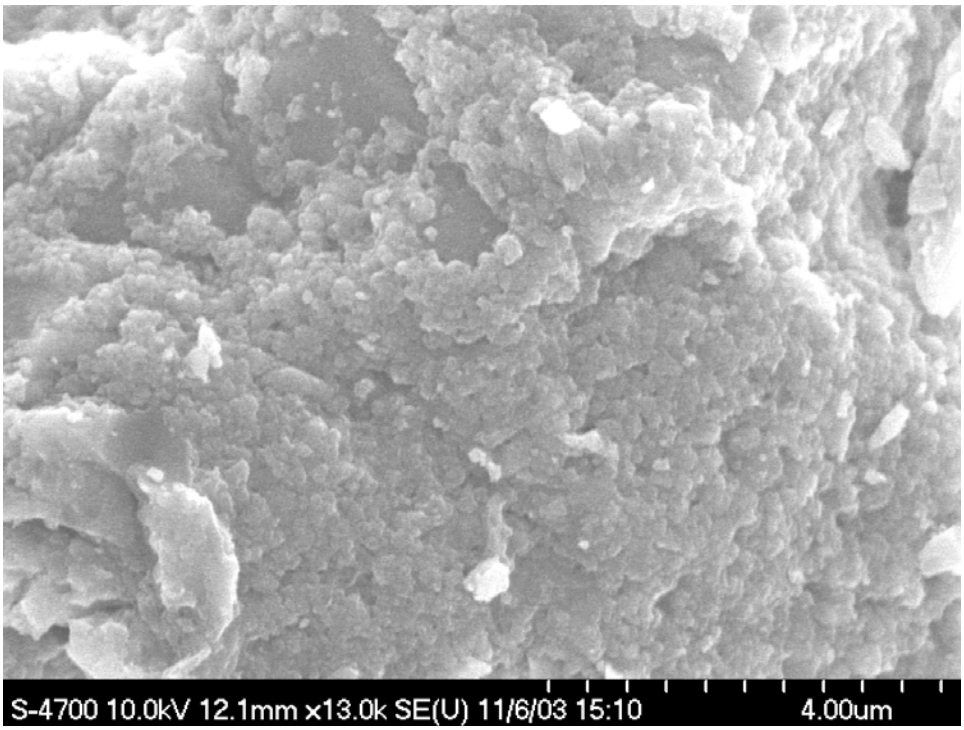


Figure 32. SEM 13 k X Magnification of a Round Particle of Recovered Catalyst of Run153

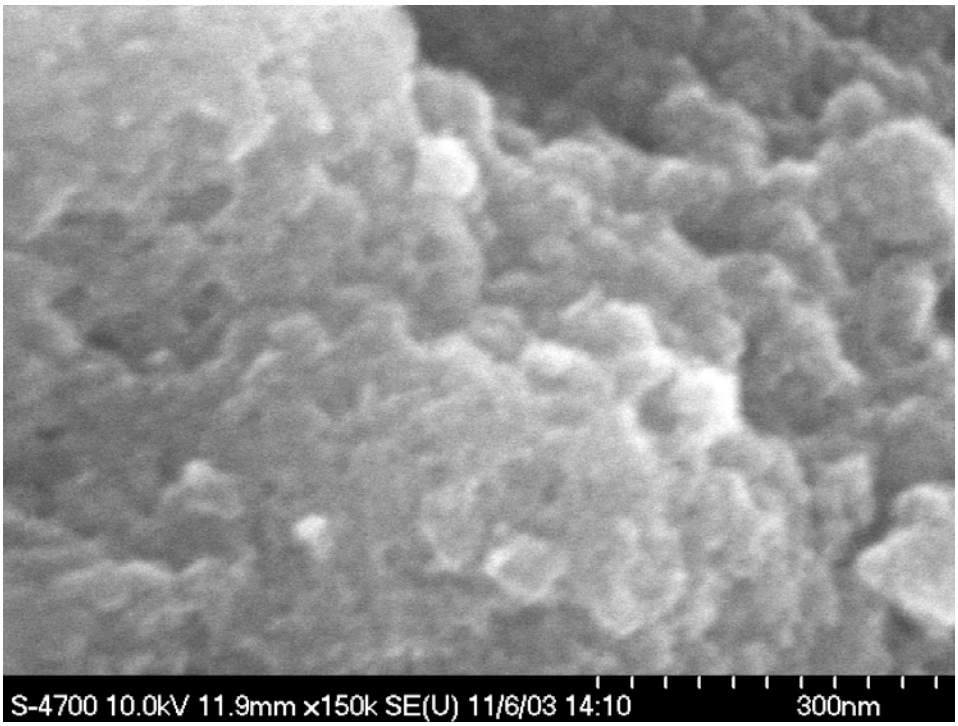


Figure 33. SEM 150 k X Magnification of a Round Particle of Recovered Catalyst of Run102

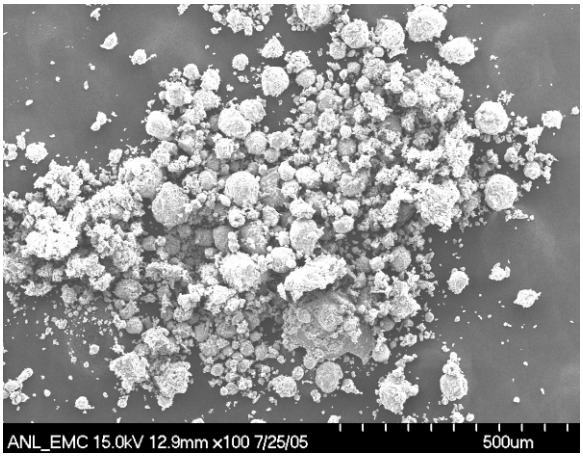


Figure 34a. Catalyst RAW_CAER_02, 100x

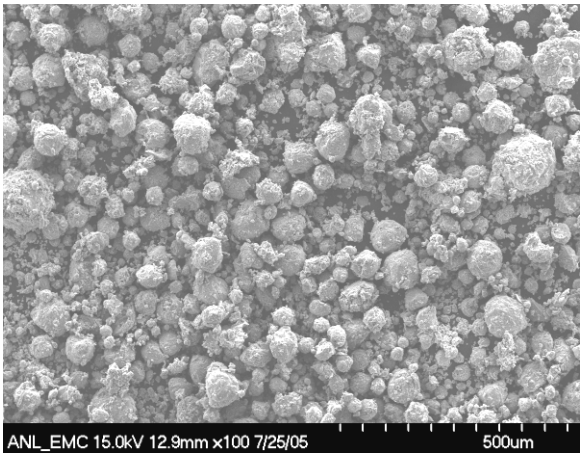


Figure 34b. Catalyst30AA_CAER_01, 100x

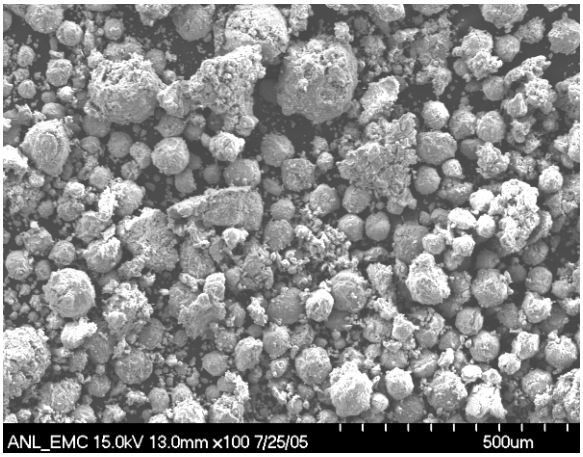


Figure 34c. Catalyst 30CC_CAER_02,

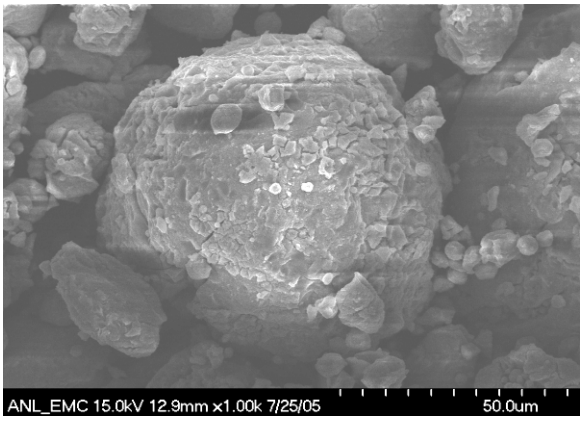


Figure 35a. Catalyst RAW_CAER_02, 1000x

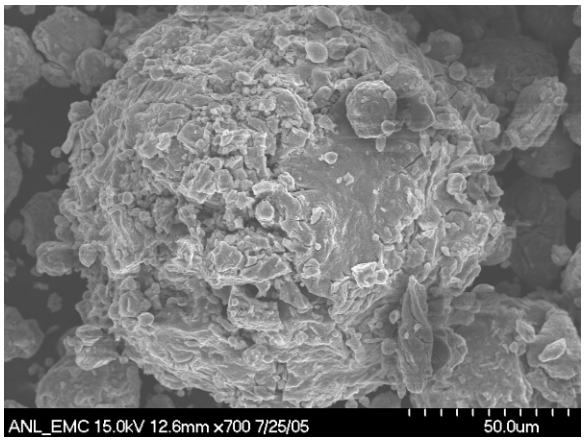


Figure 35b. Catalyst 30AA_CAER_01, 700x

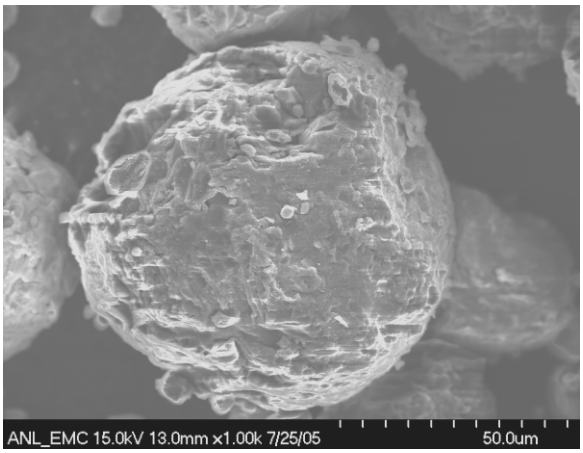


Figure 35c. Catalyst 30CC_CAER_01, 1000x

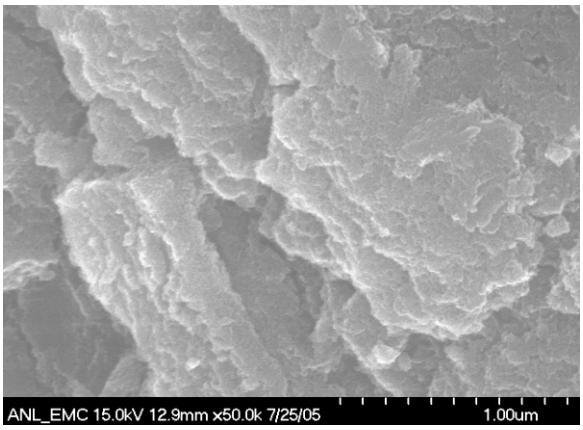


Figure 36a. Catalyst RAW_CAER_02, 50Kx

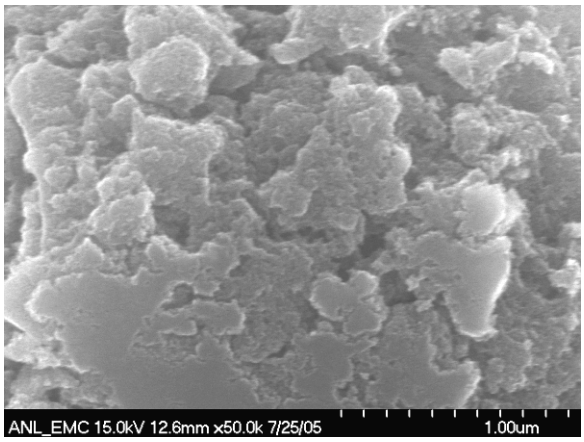


Figure 36b. Catalyst 30AA_CAER_01, 50Kx

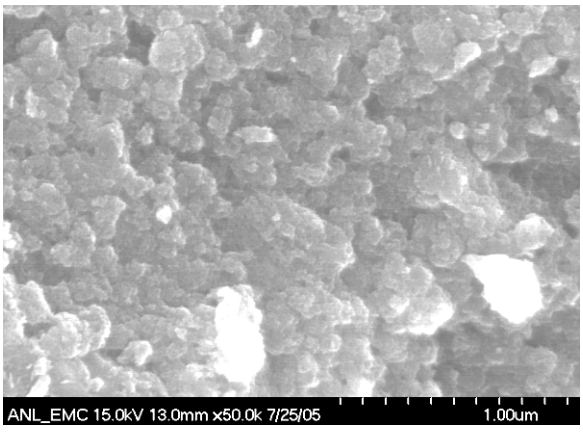


Figure 36c. Catalyst 30CC_CAER_01, 50Kx

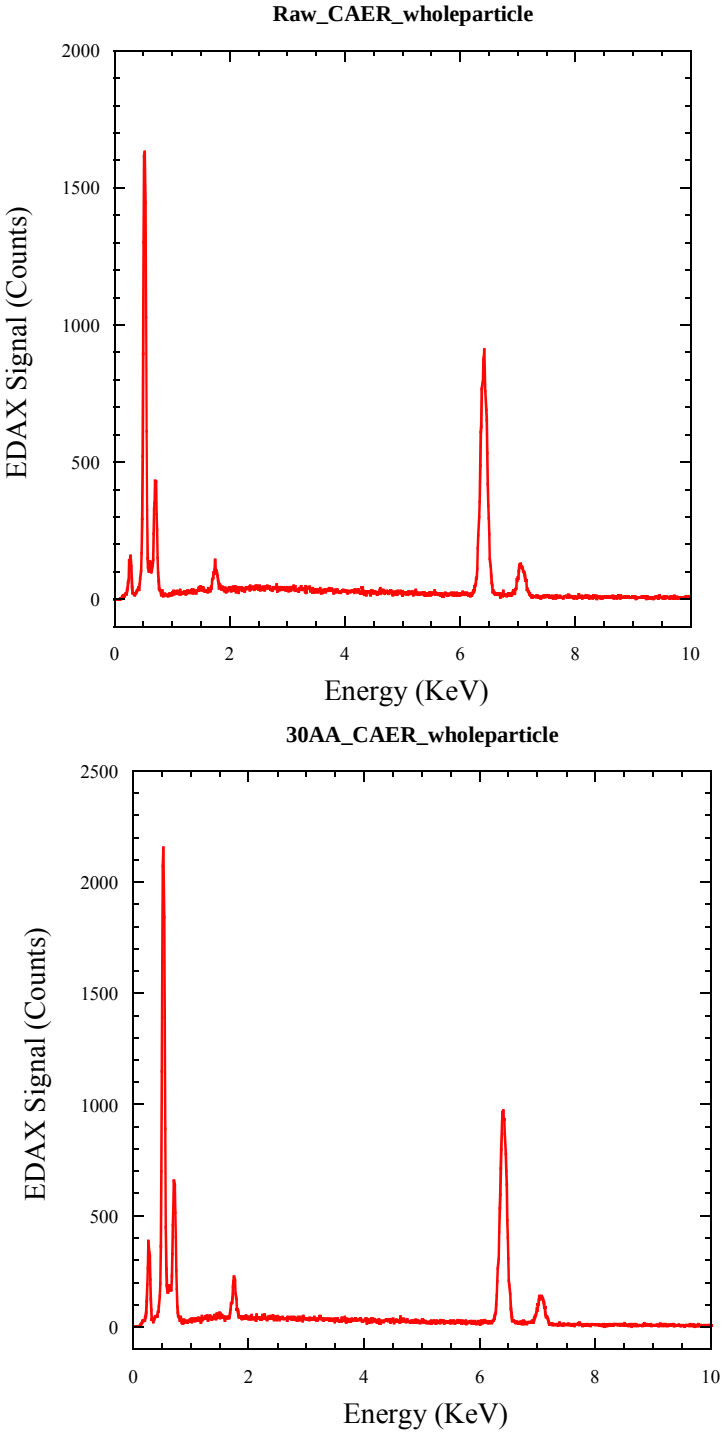


Figure 37. EDAX Spectra for Raw and 30AA_CAER Samples Transition Energies: C 0.28(K_α); O 0.53(K_α); Fe 0.62(L_L); Fe 0.71(L_α); Si 1.74(K_α); Fe 6.40(K_α); Fe 7.06(K_β)

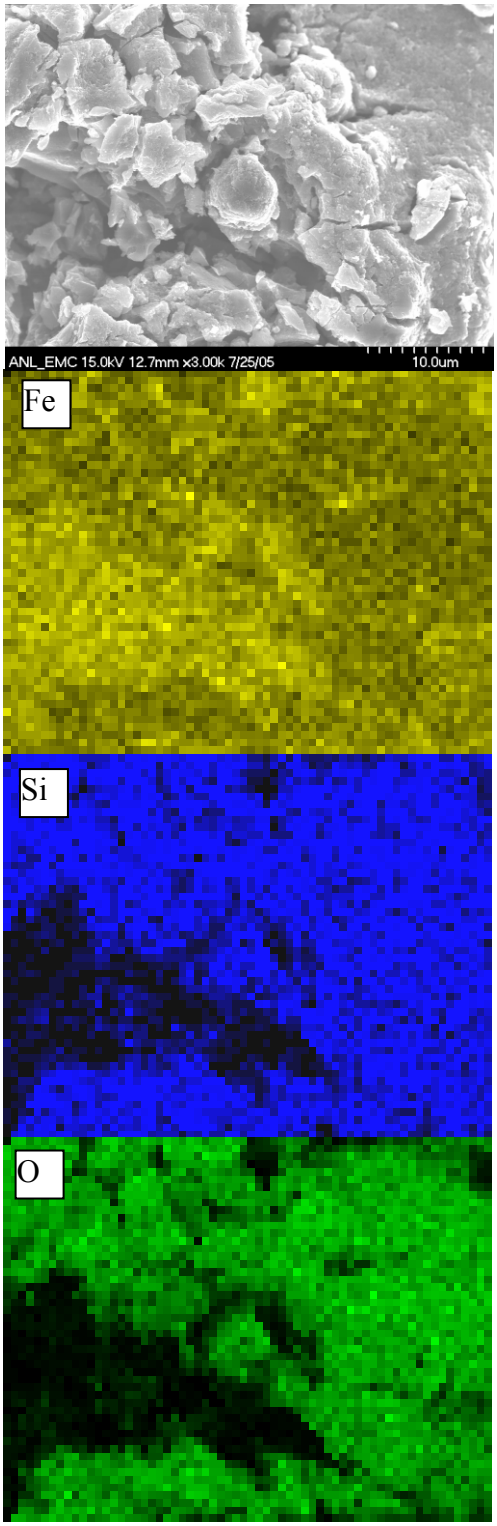


Figure 38. EDAX Elemental Maps for 30AA_CAER

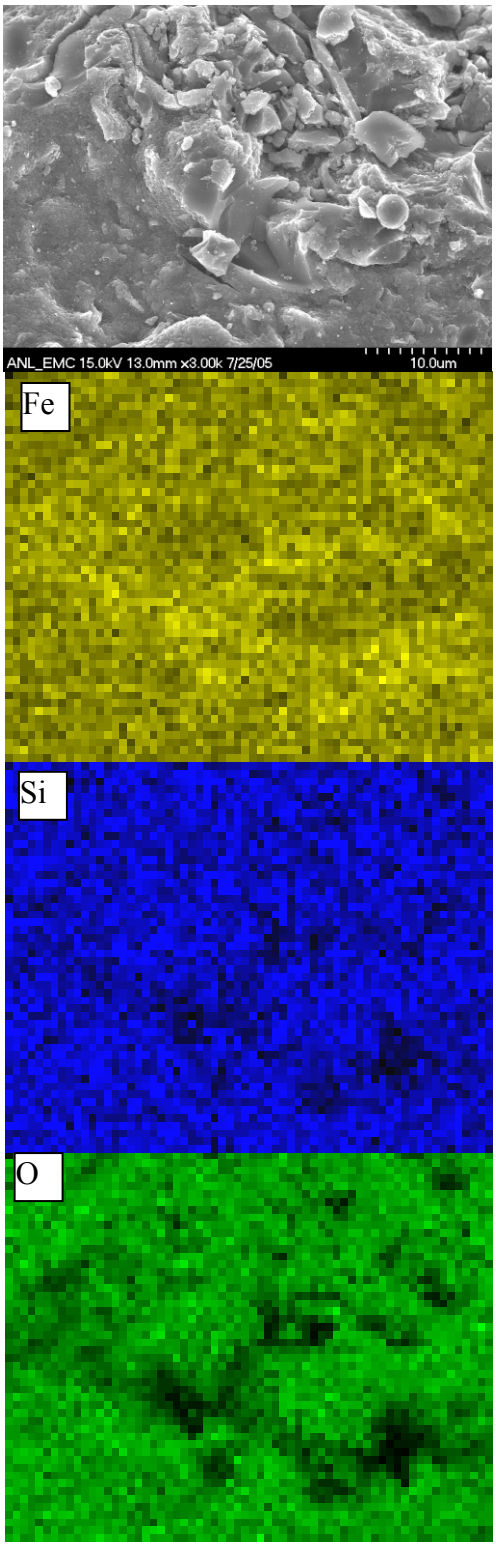


Figure 39. EDAX Elemental Maps for 30CC_CAER

Table 1

Summary of Catalysts

Catalyst Designation	Remarks/Composition
Alpha Al2O3	Inert filler
DCFT-8 & 10A	Prepared FT catalyst samples
CAER (As-Rec)	As-Received CAER Catalyst designated "RLS 4.4 Si/150 cyclone Received Aug 2000"
55-BOT	Coarse settled sample of CAER catalyst
72A, B, C	CAER Series by differential settling (A = fines, C = coarse)
77A, B	72C+TENOH+TEOS+NH4OH (77A are fines, 77B are coarse)
110A, B, C, D	CAER Series by differential settling (A = fines, D= coarse)
116A	110-D Cat + CTABr + NaSiO2 sol + EtOAc
116B	Same, but lower levels (0.1 vs. 0.28)
116C	Same as 111B, but time for solvent penetration All calcined at 500 C
132A, B, C, D, E	CAER Series by differential settling (A = fines, E = coarse)
134A	132E Cat + CTABr + NaSiO2 sol + EtOAc (CTABr=0.10g/2.5g CAER Cat)
135A	Same as 134A but lower level (CTABr=0.06g/2.5g CAER Cat)
135B	Same as 135A but CAER 132A fines (CTABr=0.06g/2.5g CAER Cat)
176A, B, C, D	CAER Series by differential settling (A = fines, D = coarse)
178A	0.113g TEOS in H2SO4/EtOH/H2O for 24 hrs at 25C then add 1.50g 176D Cat, hold at 45C for 116 hrs, filter and calcine at 500C
178B	0.113g TEOS in H2SO4/EtOH/H2O for 24 hrs at 25C, add NH4OH to pH 10.0, then add 1.50g 176D Cat, hold at 45C for 116 hrs, filter and calcine at 500C
178C	0.229g TEOS in H2SO4/EtOH/H2O for 24 hrs at 25C then add 1.51g 176D Cat, hold at 45C for 116 hrs, filter and calcine at 500C
178D	0.728g TEOS in H2SO4/EtOH/H2O for 24 hrs at 25C then add 1.50g 176D Cat, hold at 45C for 116 hrs, filter and calcine at 500C
180A	Blank: No TEOS in H2SO4/EtOH/H2O for 24 hrs at 25C then add 1.50g 176D Cat, hold at 45C for 116 hrs, filter and calcine at 500C
183A	0.114g TEOS in HCl/EtOH/H2O for 24 hrs at 25C then add 1.50g 176D Cat, hold at 45C for 116 hrs, filter and calcine at 500C
183B	0.231g TEOS in HCl/EtOH/H2O for 24 hrs at 25C then add 1.50g 176D Cat, hold at 45C for 116 hrs, filter and calcine at 500C
183C	0.465g TEOS in HCl/EtOH/H2O for 24 hrs at 25C then add 1.50g 176D Cat, hold at 45C for 116 hrs, filter and calcine at 500C
2121-30AA	(0.119g TEOS in 4.90g EtOH) + (0.097g H2O + .020g HNO3 + 2.9g EtOH) for 24 hrs at 25C hold at 45C 48 Hrs add 1.50g 110D Cat, hold at 45C for 4 days, filter and calcine at 500C
2121-30BB	(0.119g TEOS in 4.90g EtOH) + (0.097g H2O + .020g HNO3 + 2.9g EtOH) for 24 hrs at 25C add 1.49g 110D Cat, hold at 45C for 48 Hrs, filter and calcine at 500C
2121-30CC	(0.251g TEOS in 4.76g EtOH) + (0.097g H2O + .020g HNO3 + 2.9g EtOH) for 24 hrs at 25C add 1.50g 110D Cat, hold at 45C for 48 Hrs, filter and calcine at 500C

Table 2

Summary of FT Catalytic Runs

Number	Catalyst Designation	Calcination Temperature, C	FT Run Number (NB 1747 unless noted)	Run Temperature, C
1	Alpha Al2O3	----	85A	267
			87B	271
			87A	272
			85C	289
2	CAER (As-Rec)	----	100	268
			101	284
3	CAER (Coarse) (72C)	----	90	268
			96	281
			92	283
			93	286
4	77B	400	105	270
			106	288
5	116A	500	128-3,4	269
			128-6,7	285
6	116B	500	124-2,3	272
			124-5,6	291
7	116C	500	119-5,6	272
			120-4,5	288
8	134A/400	400	163 A	275
			163 B	292
9	134A/475	475	171 A	275
			171 B	288
10	135A/400	400	155 A	269
			155 B	287
11	135A/475	475	159 A	269
			159 B	287
12	135A/550	550	150 A	269
			150 B	290
13	178A	500	190A	274
			190B	287
14	178B	500	2121-4A	270
			2121-4B	293
15	178C	500	2121-7A	268
			2121-7B	289
16	178D	500	2121-9A	271
			2121-9B	287
17	180A	500	186A	272
			186B	288
18	183A	500	2121-12A	270
			2121-12B	289
19	183B	500	2121-14A	270
			2121-14B	289
20	183C	500	2121-16A	271
			2121-16B	287
21	2121-30AA	500	2121-39A	271
			2121-39B	291
22	2121-30BB	500	2121-35A	274

Table 3

Result Summary: Fischer-Tropsch Experimental Series
Runs 85 through 106

Catalyst		Run No.	Mid-Bed Temp, C	H2	CO	CO2	C1	C2	C2=	C3	C3=	C4	All C4=	C5's	C6+	SUM C1+
Alpha Al2C	Gas Analyses, %	85A	267	49.83	50.17	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Gas Analyses, %	87B	271	48.77	51.19	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05
	Gas Analyses, %	87A	272	51.91	48.08	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02
	Gas Analyses, %	85C	289	49.50	50.50	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
	Average			50.00	49.98											
CAER (As-	Gas Analyses, %	100	268	37.72	45.81	10.79	1.73	0.24	0.99	0.17	1.22	0.15	0.76	0.20	0.25	5.45
	Conversion, %				35.54	15.19	2.43	0.68	2.78	0.71	5.16	0.82	4.25	1.42	2.11	20.35
	Selectivity, %					42.74	6.84	1.90	7.83	1.98	14.51	2.30	11.96	4.00	5.94	57.26
	Gas Analyses, %	101	284	34.91	34.52	20.17	3.44	0.62	1.24	0.31	1.99	0.24	1.17	0.88	0.24	9.88
	Conversion, %				56.94	25.16	4.29	1.55	3.09	1.14	7.45	1.20	5.82	5.48	1.77	31.78
	Selectivity, %					44.18	7.53	2.72	5.42	2.00	13.08	2.10	10.22	9.62	3.11	55.82
CAER (Co	Gas Analyses, %	90	268	33.57	51.36	7.64	2.50	0.41	0.91	0.23	1.44	0.19	0.83	0.70	0.23	7.36
	Conversion, %				34.23	9.79	3.20	1.05	2.32	0.87	5.51	0.96	4.27	4.49	1.77	24.44
	Selectivity, %					28.60	9.36	3.06	6.77	2.54	16.10	2.81	12.46	13.13	5.16	71.40
	Gas Analyses, %	96	281	34.57	47.08	9.77	3.44	0.59	0.86	0.27	1.55	0.17	0.83	0.68	0.20	8.59
	Conversion, %				39.06	12.65	4.45	1.53	2.24	1.03	6.01	0.87	4.31	4.41	1.55	26.42
	Selectivity, %					32.37	11.40	3.92	5.73	2.64	15.38	2.24	11.04	11.30	3.98	67.63
	Gas Analyses, %	92	283	27.15	45.92	16.00	4.03	0.70	1.21	0.32	2.11	0.24	1.28	0.79	0.24	11.07
	Conversion, %				48.15	18.07	4.55	1.58	2.72	1.09	7.15	1.08	5.80	4.47	1.64	30.09
	Selectivity, %					37.52	9.45	3.28	5.66	2.27	14.84	2.25	12.04	9.29	3.40	62.48
	Gas Analyses, %	93	286	28.81	45.67	13.97	4.28	0.75	1.11	0.33	2.00	0.24	1.20	0.84	0.23	10.74
	Conversion, %				46.87	16.25	4.98	1.73	2.58	1.15	6.96	1.12	5.60	4.88	1.63	30.62
	Selectivity, %					34.66	10.62	3.70	5.50	2.46	14.86	2.38	11.94	10.41	3.47	65.34
DCFT-77B	Gas Analyses, %	105	270	39.48	55.91	1.44	1.25	0.14	0.32	0.09	0.55	0.09	0.24	0.29	0.28	2.96
	Conversion, %				15.17	2.19	1.89	0.41	0.97	0.42	2.49	0.53	1.47	2.22	2.58	12.99
	Selectivity, %					14.42	12.45	2.70	6.42	2.79	16.41	3.48	9.72	14.65	16.98	85.58
	Gas Analyses, %	106	288	38.49	52.73	4.23	2.16	0.26	0.55	0.15	0.90	0.13	0.64	0.45	0.17	5.23
	Conversion, %				24.88	6.03	3.08	0.74	1.55	0.63	3.85	0.72	3.62	3.19	1.45	18.85
	Selectivity, %					24.22	12.38	2.99	6.24	2.54	15.48	2.91	14.57	12.83	5.84	75.78

Notes: 1. Gas analyses is reported as mol % normalized to N2 and O2 free
2. Conversion reported as mol % of the feed carbon in CO converted to the various components.
3. Selectivity is reported as the % of the reacted carbon in feed CO that was converted to the various components.

Table 4

Result Summary: Fischer-Tropsch Experimental Series
Runs 119 through 128
File -- N:/DCC_ANL/FT_FETC/Data&Results/run_sum2.xls

Catalyst		Run No.	Mid-Bed Temp, C	H2	CO			C2	C2=	C3	C3=	C4	All C4=	C5's	C6+
116C Treated CAER	Gas Analyses, %	119-5,6	272	43.23	52.40	1.56	1.03	0.10	0.33	0.07	0.45	0.07	0.31	0.11	0.33
	Conversion, %				14.78	2.54	1.68	0.32	1.07	0.36	2.19	0.44	2.00	0.93	3.26
	Selectivity, %					17.21	11.37	2.13	7.24	2.41	14.82	2.99	13.51	6.27	22.05
	Gas Analyses, %	120-4,5	288	41.05	50.62	3.69	1.70	0.24	0.55	0.13	0.79	0.11	0.53	0.51	0.12
	Conversion, %				23.49	5.57	2.56	0.73	1.66	0.58	3.59	0.66	3.20	3.88	1.08
	Selectivity, %					23.71	10.90	3.09	7.05	2.45	15.28	2.80	13.61	16.50	4.59
116B Treated CAER	Gas Analyses, %	124-2&3	272	45.23	52.83	0.55	0.57	0.04	0.09	0.03	0.22	0.03	0.16	0.13	0.14
	Conversion, %				7.59	0.96	1.00	0.13	0.33	0.17	1.13	0.23	1.12	1.09	1.43
	Selectivity, %					12.61	13.19	1.66	4.29	2.28	14.94	3.04	14.76	14.41	18.81
	Gas Analyses, %	124-5&6	291	42.80	52.71	1.65	1.00	0.09	0.32	0.06	0.44	0.05	0.31	0.24	0.31
	Conversion, %				15.21	2.65	1.61	0.28	1.04	0.30	2.13	0.32	1.99	1.94	2.96
	Selectivity, %					17.42	10.61	1.82	6.81	1.97	14.02	2.07	13.07	12.74	19.48
116A Treated CAER	Gas Analyses, %	128-3&4	269	43.64	52.78	1.16	0.96	0.04	0.29	0.07	0.40	0.06	0.26	0.21	0.09
	Conversion, %				11.87	1.93	1.61	0.14	0.98	0.34	2.02	0.43	1.74	1.75	0.94
	Selectivity, %					16.27	13.54	1.15	8.21	2.83	17.00	3.60	14.68	14.77	7.93
	Gas Analyses, %	128-6&7	285	40.15	52.53	3.18	1.62	0.17	0.49	0.11	0.73	0.10	0.61	0.36	0.12
	Conversion, %				20.96	4.78	2.44	0.50	1.47	0.49	3.30	0.57	3.68	2.69	1.05
	Selectivity, %					22.79	11.62	2.37	7.02	2.33	15.72	2.73	17.57	12.85	5.00

Notes: 1. Gas analyses is reported as mol % normalized to N2 and O2 free
2. Conversion reported as mol % of the feed carbon in CO converted to the various components.
3. Selectivity is reported as the % of the reacted carbon in feed CO that was converted to the various components.

Table 5

Result Summary: Fischer-Tropsch Experimental Series
Runs 150 through 171
File -- N:/DCC_ANL/FT_FETC/Data&Results/run_sum3.xls

Catalyst Evaluated		Run No.	Mid-Bed Temp, C	H2	CO	CO2	C1	C2	C2=	C3	C3=	C4	All C4=	C5's	C6+
135A/550	Gas Analyses, %	150-C,D	269	32.44	50.34	11.58	2.18	0.55	0.52	0.16	1.03	0.11	0.57	0.46	0.22
(Treated CAER)	Conversion, %				33.90	15.20	2.86	1.44	1.37	0.64	4.06	0.57	3.01	3.02	1.73
	Selectivity, %					44.84	8.45	4.24	4.05	1.88	11.97	1.69	8.89	8.91	5.09
	Gas Analyses, %	150-G,H	290	28.87	37.98	24.89	3.51	0.87	0.71	0.24	1.50	0.14	1.14	0.58	0.22
	Conversion, %				54.85	29.59	4.18	2.07	1.69	0.86	5.34	0.66	5.40	3.47	1.58
	Selectivity, %					53.96	7.62	3.77	3.07	1.57	9.74	1.20	9.85	6.33	2.89
135A/400	Gas Analyses, %	155-C,D	271	36.41	52.94	6.27	1.79	0.35	0.41	0.11	0.71	0.08	0.53	0.32	0.21
(Treated CAER)	Conversion, %				24.62	8.92	2.55	1.00	1.16	0.47	3.01	0.44	3.00	2.29	1.78
	Selectivity, %					36.23	10.37	4.07	4.71	1.89	12.23	1.80	12.17	9.31	7.22
	Gas Analyses, %	155-F,G	288	32.44	44.25	16.50	3.14	0.64	0.67	0.17	1.21	0.11	0.65	0.50	0.18
	Conversion, %				42.69	21.37	4.07	1.64	1.73	0.66	4.69	0.56	3.34	3.23	1.39
	Selectivity, %					50.06	9.53	3.85	4.04	1.54	11.00	1.32	7.83	7.57	3.26
135A/475	Gas Analyses, %	159-C,D	269	33.67	53.55	7.79	1.97	0.42	0.49	0.13	0.86	0.09	0.51	0.41	0.19
(Treated CAER)	Conversion, %				27.30	10.57	2.67	1.14	1.32	0.53	3.49	0.51	2.77	2.77	1.53
	Selectivity, %					38.71	9.80	4.19	4.82	1.94	12.77	1.85	10.16	10.14	5.61
	Gas Analyses, %	159-G,H	287	28.62	41.15	22.46	3.54	0.75	0.81	0.21	1.48	0.13	0.74	0.57	0.21
	Conversion, %				50.37	27.09	4.27	1.81	1.95	0.74	5.34	0.60	3.58	3.46	1.53
	Selectivity, %					53.78	8.48	3.60	3.87	1.47	10.60	1.20	7.12	6.86	3.03
134A/400	Gas Analyses, %	163-C,D	275	37.01	54.76	4.56	1.50	0.30	0.31	0.09	0.57	0.07	0.43	0.29	0.19
(Treated CAER)	Conversion, %				20.14	6.66	2.19	0.86	0.91	0.41	2.49	0.41	2.50	2.09	1.63
	Selectivity, %					33.05	10.88	4.27	4.52	2.02	12.38	2.03	12.40	10.36	8.08
	Gas Analyses, %	163-F,G	292	31.99	48.97	12.91	2.69	0.53	0.54	0.15	1.04	0.10	0.59	0.78	0.31
	Conversion, %				37.82	16.39	3.41	1.35	1.38	0.57	3.95	0.49	2.99	4.94	2.35
	Selectivity, %					43.34	9.03	3.57	3.64	1.51	10.44	1.29	7.90	13.06	6.23
134A/475	Gas Analyses, %	171-B,C	275	36.73	53.52	5.48	1.84	0.35	0.37	0.10	0.67	0.07	0.42	0.32	0.20
(Treated CAER)	Conversion, %				22.78	7.91	2.66	1.01	1.08	0.45	2.88	0.43	2.40	2.28	1.71
	Selectivity, %					34.70	11.66	4.42	4.74	1.96	12.65	1.87	10.51	10.01	7.49
	Gas Analyses, %	171-E,F	288	33.64	50.09	10.83	2.67	0.51	0.52	0.14	0.95	0.09	0.57	0.40	0.21
	Conversion, %				33.03	14.48	3.56	1.37	1.40	0.54	3.80	0.47	3.02	2.67	1.72
	Selectivity, %					43.84	10.79	4.15	4.23	1.64	11.50	1.43	9.15	8.08	5.20

Notes: 1. Gas analyses is reported as mol % normalized to N2 and O2 free
2. Conversion reported as mol % of the feed carbon in CO converted to the various components.
3. Selectivity is reported as the % of the reacted carbon in feed CO that was converted to the various components.

Table 6

Result Summary: Fischer-Tropsch Experimental Series
Runs 186 through 2121-9
File -- N:/DCC_ANL/FT_FETC/Data&Results/run_sum4.xls

Catalyst Evaluated		Run No.	Mid-Bed Temp, C	H2	CO	CO2	C1	C2	C2=	C3	C3=	C4	All C4=	C5's	C6+
180A	Gas Analyses, %	186-A	272	47.96	51.18	0.22	0.34	0.10	0.03	0.03	0.06	0.01	0.03	0.02	0.04
	Conversion, %				3.03	0.42	0.64	0.38	0.12	0.19	0.32	0.11	0.20	0.21	0.45
	Selectivity, %					13.87	20.99	12.37	3.87	6.37	10.68	3.50	6.50	6.87	14.99
	Gas Analyses, %	186-B	288	45.42	50.54	3.33	0.58	0.18	0.06	0.06	0.10	0.02	0.03	0.05	0.04
	Conversion, %				9.92	5.93	1.03	0.63	0.20	0.32	0.55	0.17	0.24	0.42	0.43
	Selectivity, %					59.77	10.37	6.36	2.01	3.23	5.55	1.72	2.44	4.22	4.31
178A	Gas Analyses, %	190-A	274	46.48	51.17	1.59	0.36	0.11	0.03	0.04	0.06	0.02	0.03	0.07	0.21
	Conversion, %				7.83	2.87	0.64	0.40	0.12	0.23	0.34	0.13	0.24	0.59	2.25
	Selectivity, %					36.69	8.22	5.11	1.57	2.97	4.35	1.66	3.13	7.59	28.72
	Gas Analyses, %	190-B	287	46.58	51.36	0.83	0.63	0.23	0.06	0.08	0.11	0.03	0.03	0.05	0.07
	Conversion, %				5.60	1.46	1.11	0.79	0.19	0.40	0.59	0.18	0.26	0.40	0.22
	Selectivity, %					26.01	19.85	14.13	3.47	7.13	10.50	3.21	4.62	7.23	3.85
178B	Gas Analyses, %	2121-4A	270	47.35	51.67	0.27	0.35	0.11	0.04	0.04	0.07	0.02	0.03	0.03	0.03
	Conversion, %				3.27	0.51	0.65	0.41	0.13	0.22	0.39	0.12	0.25	0.32	0.28
	Selectivity, %					15.55	19.78	12.46	4.00	6.69	12.01	3.66	7.55	9.72	8.58
	Gas Analyses, %	2121-4B	293	45.74	51.31	0.80	0.31	0.07	0.06	0.11	0.15	0.04	0.08	0.08	0.05
	Conversion, %				6.02	1.46	0.56	0.24	0.23	0.59	0.82	0.27	0.57	0.73	0.54
	Selectivity, %					24.20	9.36	4.01	3.89	9.85	13.59	4.50	9.49	12.16	8.94
178C	Gas Analyses, %	2121-7A	268	46.63	52.50	0.20	0.28	0.10	0.03	0.03	0.06	0.01	0.10	0.03	0.05
	Conversion, %				3.52	0.37	0.51	0.37	0.12	0.19	0.31	0.10	0.76	0.27	0.52
	Selectivity, %					10.45	14.53	10.56	3.35	5.33	8.78	2.93	21.75	7.58	14.74
	Gas Analyses, %	2121-7B	289	45.60	51.77	1.16	0.72	0.26	0.06	0.09	0.13	0.03	0.07	0.08	0.05
	Conversion, %				7.58	2.07	1.28	0.92	0.21	0.47	0.70	0.22	0.46	0.68	0.56
	Selectivity, %					27.35	16.93	12.10	2.82	6.21	9.25	2.92	6.12	8.95	7.34
178D	Gas Analyses, %	2121-9A	271	39.41	49.84	6.53	1.81	0.89	0.09	0.44	0.38	0.15	0.26	0.18	0.16
	Conversion, %				24.52	9.89	2.74	2.68	0.26	2.00	1.70	0.88	1.59	1.33	1.44
	Selectivity, %					40.35	11.18	10.94	1.06	8.15	6.95	3.58	6.47	5.43	5.89
	Gas Analyses, %	2121-9B	287	31.08	38.67	18.39	3.74	2.07	0.09	1.22	3.03	0.39	0.26	0.51	0.28
	Conversion, %				54.34	21.71	4.42	4.88	0.22	4.33	10.73	1.85	1.24	3.00	1.96
	Selectivity, %					39.96	8.13	8.98	0.40	7.97	19.74	3.41	2.29	5.52	3.61

Notes: 1. Gas analyses is reported as mol % normalized to N2 and O2 free
2. Conversion reported as mol % of the feed carbon in CO converted to the various components.
3. Selectivity is reported as the % of the reacted carbon in feed CO that was converted to the various components.

Table 7

Result Summary: Fischer-Tropsch Experimental Series
Runs 2121-12A through 2121-16B
File -- N:/DCC_ANL/FT_FETC/Data&Results/run_sum5.xls

Catalyst Evaluated		Run No. (2121-)	Mid-Bed Temp, C	H2	CO	CO2	C1	C2	C2=	C3	C3=	C4	All C4=	C5's	C6+	SUM C1+
183A	Gas Analyses, %	12A	270	31.98	53.33	9.23	1.99	0.45	0.54	0.15	1.00	0.10	0.62	0.56	0.25	5.66
	Conversion, %				30.87	11.96	2.58	1.18	1.41	0.58	3.88	0.53	3.19	3.65	1.92	18.91
	Selectivity, %					38.75	8.35	3.81	4.56	1.86	12.56	1.73	10.34	11.82	6.22	61.25
	Gas Analyses, %	12B	289	24.30	36.00	19.41	3.34	0.75	0.89	0.21	1.60	0.12	0.90	0.70	0.26	8.76
	Conversion, %				53.00	25.34	4.35	1.95	2.33	0.81	6.27	0.65	4.70	4.58	2.03	27.66
	Selectivity, %					47.81	8.22	3.68	4.40	1.52	11.83	1.22	8.86	8.63	3.83	52.19
183B	Gas Analyses, %	14A	270	39.28	55.07	2.87	1.18	0.25	0.26	0.08	0.24	0.06	0.32	0.22	0.19	2.79
	Conversion, %				15.06	4.43	1.81	0.76	0.79	0.37	1.13	0.36	1.97	1.69	1.75	10.63
	Selectivity, %					29.41	12.04	5.06	5.22	2.49	7.50	2.38	13.07	11.21	11.61	70.59
	Gas Analyses, %	14B	289	34.95	50.94	9.12	2.14	0.44	0.46	0.13	0.90	0.08	0.55	0.41	0.23	5.35
	Conversion, %				30.27	12.48	2.93	1.21	1.27	0.53	3.70	0.46	3.01	2.83	1.85	17.79
	Selectivity, %					41.24	9.69	4.01	4.20	1.74	12.21	1.52	9.95	9.36	6.10	58.76
183C	Gas Analyses, %	16A	271	39.39	55.21	2.69	1.20	0.24	0.24	0.08	0.24	0.06	0.27	0.24	0.18	2.74
	Conversion, %				14.53	4.16	1.86	0.73	0.75	0.36	1.11	0.36	1.68	1.88	1.64	10.37
	Selectivity, %					28.61	12.79	5.01	5.18	2.46	7.67	2.47	11.55	12.95	11.32	71.39
	Gas Analyses, %	16B	287	36.00	52.38	7.16	1.97	0.36	0.40	0.10	0.71	0.06	0.41	0.28	0.14	4.43
	Conversion, %				24.72	10.28	2.83	1.04	1.14	0.42	3.07	0.36	2.35	2.04	1.19	14.44
	Selectivity, %					41.60	11.45	4.21	4.62	1.69	12.40	1.47	9.49	8.26	4.81	58.40

Notes: 1. Gas analyses is reported as mol % normalized to N2 and O2 free
2. Conversion reported as mol % of the feed carbon in CO converted to the various components.
3. Selectivity is reported as the % of the reacted carbon in feed CO that was converted to the various components.

Table 8

Result Summary: Fischer-Tropsch Experimental Series
Runs 2121-35A through 2121-41B
File -- N:/DCC_ANL/FT_FETC/Data&Results/run_sum6.xls

Catalyst Evaluated		Run No. (2121-)	Mid-Bed Temp, C	H2	CO	CO2	C1	C2	C2=	C3	C3=	C4	All C4=	C5's	C6+	SUM C1+
2121-30BB	Gas Analyses, %	35A	274	30.31	42.65	19.37	2.67	0.68	0.62	0.20	1.29	0.12	0.84	0.53	0.19	7.14
	Conversion, %				46.27	24.40	3.37	1.70	1.57	0.75	4.88	0.59	4.21	3.35	1.45	21.87
	Selectivity, %					52.74	7.28	3.68	3.40	1.61	10.54	1.28	9.10	7.24	3.14	47.26
	Gas Analyses, %	35B	293	26.35	25.61	38.76	4.49	1.18	0.79	0.33	1.89	0.16	0.96	0.56	0.18	10.55
	Conversion, %				70.85	44.11	5.11	2.69	1.80	1.11	6.45	0.74	4.37	3.21	1.24	26.74
	Selectivity, %					62.26	7.22	3.80	2.54	1.57	9.11	1.05	6.16	4.53	1.76	37.74
2121-30AA	Gas Analyses, %	39A	271	34.30	50.48	10.48	1.90	0.42	0.45	0.14	0.86	0.09	0.55	0.34	0.25	4.98
	Conversion, %				31.12	14.30	2.59	1.14	1.23	0.55	3.51	0.50	2.98	2.29	2.03	16.82
	Selectivity, %					45.94	8.33	3.67	3.94	1.78	11.28	1.60	9.58	7.36	6.51	54.06
	Gas Analyses, %	39B	291	28.51	32.83	29.80	3.69	0.84	0.77	0.23	1.58	0.69	0.84	0.48	0.23	9.36
	Conversion, %				61.34	35.09	4.34	1.99	1.81	0.83	5.59	3.24	3.97	2.83	1.65	26.25
	Selectivity, %					57.21	7.08	3.24	2.95	1.35	9.11	5.28	6.48	4.62	2.68	42.79
2121-30CC	Gas Analyses, %	41A	271	38.29	54.17	4.11	1.37	0.27	0.30	0.09	0.54	0.06	0.35	0.23	0.23	3.43
	Conversion, %				18.90	6.15	2.06	0.80	0.88	0.39	2.41	0.37	2.12	1.71	2.03	12.75
	Selectivity, %					32.53	10.88	4.23	4.68	2.05	12.73	1.94	11.21	9.03	10.72	67.47
	Gas Analyses, %	41B	287	33.33	50.43	11.01	2.24	0.44	0.46	0.13	0.88	0.25	0.59	0.32	0.22	5.52
	Conversion, %				32.51	14.74	2.99	1.19	1.24	0.51	3.51	1.33	3.14	2.12	1.73	17.77
	Selectivity, %					45.33	9.21	3.65	3.81	1.58	10.81	4.11	9.66	6.53	5.31	54.67

Notes: 1. Gas analyses is reported as mol % normalized to N2 and O2 free
2. Conversion reported as mol % of the feed carbon in CO converted to the various components.
3. Selectivity is reported as the % of the reacted carbon in feed CO that was converted to the various components.

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